Universidade de Aveiro Departamento de Química
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Ana Luísa Carvalho Magalhães

Coeficientes de Difusão em Fluidos Densos e Supercríticos

Diffusion Coefficients in Dense and Supercritical Fluids

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Engenharia Química, realizada sob a orientação científica do Doutor Carlos Manuel Santos Silva, Professor Auxiliar do Departamento de Química da Universidade de Aveiro, e do Doutor Francisco Avelino Da Silva Freitas, Professor Auxiliar do Departamento de Química da Universidade de Aveiro.

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Dedico este trabalho aos meus queridos pais.

O júri

Presidente	Professor José Rodrigues Ferreira da Rocha Professor Catedrático da Universidade de Aveiro
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	Doutor Carlos Manuel Santos da Silva Professor Auxiliar da Universidade de Aveiro

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Palavras-chave

Coeficiente de difusão, propriedade de transporte, modelação, correlação, previsão, fluido denso, fluido supercrítico, cromatografia de abertura de pico

Resumo

Os coeficientes de difusão (D_{12}) são propriedades fundamentais na investigação e na indústria, mas a falta de dados experimentais e a inexistência de equações que os estimem com precisão e confiança em fases comprimidas ou condensadas constituem limitações importantes.

Os objetivos principais deste trabalho compreendem: *i*) a compilação de uma grande base de dados para valores de D_{12} de sistemas gasosos, líquidos e supercríticos; *ii*) o desenvolvimento e validação de novos modelos de coeficientes de difusão a diluição infinita, aplicáveis em amplas gamas de temperatura e densidade, para sistemas contendo componentes muito distintos em termos de polaridade, tamanho e simetria; *iii*) a montagem e teste de uma instalação experimental para medir coeficientes de difusão em líquidos e fluidos supercríticos.

Relativamente à modelação, uma nova expressão para coeficientes de difusão a diluição infinita de esferas rígidas foi desenvolvida e validada usando dados de dinâmica molecular (desvio relativo absoluto médio, AARD = 4.44%)

Foram também estudados os coeficientes de difusão binários de sistemas reais. Para tal, foi compilada uma extensa base de dados de difusividades de sistemas reais em gases e solventes densos (622 sistemas binários num total de 9407 pontos experimentais e 358 moléculas) e a mesma foi usada na validação dos novos modelos desenvolvidos nesta tese.

Um conjunto de novos modelos foi proposto para o cálculo de coeficientes de difusão a diluição infinita usando diferentes abordagens: *i*) dois modelos de base molecular com um parâmetro específico para cada sistema, aplicáveis em sistemas gasosos, líquidos e supercríticos, em que natureza do solvente se encontra limitada a apolar ou fracamente polar (AARDs globais na gama 4.26-4.40%); *ii*) dois modelos de base molecular biparamétricos, aplicáveis em todos os estados físicos, para qualquer tipo de soluto diluído em qualquer solvente (apolar, fracamente polar e polar). Ambos os modelos dão origem a erros globais entre 2.74% e 3.65%; *iii*) uma correlação com um parâmetro, específica para coeficientes de difusão em dióxido de carbono supercrítico (SC-CO_2) e água líquida (AARD = 3.56%); *iv*) nove correlações empíricas e semi-empíricas que envolvem dois parâmetros, dependentes apenas da temperatura e/ou densidade do solvente e/ou viscosidade do solvente. Estes últimos modelos são muito simples e exibem excelentes resultados (AARDs entre 2.78% e 4.44%) em sistemas líquidos e supercríticos; e *v*) duas equações preditivas para difusividades de solutos em SC-CO_2, em que os erros globais de ambas são inferiores a 6.80%.

No global, deve realçar-se o facto de os novos modelos abrangerem a grande variedade de sistemas e moléculas geralmente encontrados. Os resultados obtidos são consistentemente melhores do que os obtidos com os modelos e abordagens encontrados na literatura. No caso das correlações

com um ou dois parâmetros, mostrou-se que estes mesmos parâmetros podem ser ajustados usando um conjunto muito pequeno de dados, e posteriormente serem utilizados na previsão de valores de D_{12} longe do conjunto original de pontos.

Uma nova instalação experimental para medir coeficientes de difusão binários por técnicas cromatográficas foi montada e testada. O equipamento, o procedimento experimental e os cálculos analíticos necessários à obtenção dos valores de D_{12} pelo método de abertura do pico cromatográfico, foram avaliados através da medição de difusividades de tolueno e acetona em SC-CO_2. Seguidamente, foram medidos coeficientes de difusão de eucaliptol em SC-CO_2 nas gamas de 202 – 252 bar e 313.15 – 333.15 K. Os resultados experimentais foram analisados através de correlações e modelos preditivos para D_{12}.

Keywords

Diffusion coefficient, transport property, modelling, correlation, prediction, dense fluid, supercritical fluid, chromatographic peak broadening

Abstract

Diffusivities (D_{12}) are fundamental properties both at research and industry levels, but the lack of experimental data and the non-existence of reliable and accurate equations to estimate them in compressed and condensed phases constitute important shortcomings.

The main objectives of this work comprise: *i*) the compilation of a large database of D_{12} values in gas, liquid and supercritical systems; *ii*) the development and validation of new models for tracer diffusivities, applicable over wide ranges of temperature and density, for systems containing very distinct components in term of polarity, size and symmetry; *iii*) the installation and test of an experimental set-up to measure diffusion coefficients in liquids and supercritical fluids.

Concerning modelling, a new accurate expression for tracer diffusion coefficients of hard sphere fluid was developed and validated using molecular dynamic data (average absolute relative deviation, AARD = 4.44%).

The binary diffusion coefficients of real systems were also studied. An extensive database of diffusivities in gas and dense solvents was compiled (622 binary systems performing 9407 data points and comprehending 358 molecules) and used to validate the new models developed in this thesis.

A set of new models were proposed for tracer diffusivities using different approaches: *i*) two molecularly-based models with one system-specific parameter that are applicable to gas, liquid, and supercritical systems, where the nature of solvent is limited to non-polar or weakly polar (global AARDs in the range 4.26-4.40%); *ii*) two molecularly-based models with two parameters, applicable in all physical states, for any solutes diluted in any type of solvent (non-polar, weakly-polar, and polar). Both models provide global errors between 2.74% and 3.65%; *iii*) one correlation with one parameter devoted to D_{12} coefficients in supercritical carbon dioxide (SC-CO_2) and liquid water (AARD = 3.56%); *iv*) nine empirical and semi-empirical correlations involving two parameters, dependent on temperature and/or solvent density and/or solvent viscosity. These models are very simple and provide accurate results (AARDs between 2.78% and 4.44%) in liquid and supercritical systems; and *v*) two predictive equations for diffusivities of solutes in SC-CO_2 where the global deviations for both are inferior to 6.80%.

In the whole, it may be emphasized that the new models cover the large variety of systems and molecules generally found. The results achieved are consistently better than those obtained by well known models and approaches taken from the literature. In the case of the 1- and 2-parameter correlations, it has been shown that such parameters can be fitted to a very small set of data, and subsequently used to predict D_{12} values far from the original set of points.

A new experimental set-up to measure binary diffusion coefficients by chromatographic techniques was designed and tested. The equipment, experimental procedure and analytical calculations to obtain the D_{12} values by the chromatographic peak broadening technique were assessed by measuring diffusivities of toluene and acetone in SC-CO_2. Then, the diffusivities of eucalyptol in SC-CO_2 were determined in the ranges 202 – 252 bar and 313.15 – 333.15 K. The experimental data were analysed using D_{12} predictive and correlation models.

Index

Part I. Modelling

Part II. Experimental Section

List of Figures

Chapter 2

Chapter 4

Paper I

Paper II

Paper III

Paper IV

Paper V

Paper VI

Paper VII

Paper VIII

Chapter 5

Chapter 6

List of Tables

Chapter 2

Chapter 3

Chapter 4

Paper I

Paper II

Paper III

Paper IV

Paper V

Paper VI

Paper VII

Paper VIII

Chapter 6

1. Introduction

Diffusion is a microscopic level phenomenon that results from particles motion and interaction between them. The diffusion coefficient, in macroscopical terms, is defined as the proportionality constant between particles flux and chemical potential [1-2], being fundamental in different engineering and industrial applications, to design and/or simulate processes involving mass transfer (*e.g.* multiphase reactors, liquid-liquid and supercritical extractors, distillation and absorption, adsorption and membranes, etc.) [3-7]. These coefficients can be experimentally measured, calculated via computer simulations, or estimated by macroscopic models.

The infinitely dilute diffusion coefficient of a solute in a solvent, D_{12}, is one of the most important transport properties and its importance is not restricted to systems at infinite dilution, but also for concentrated solutions, whether binary or multicomponent, where the implied effective diffusivities can be estimated on the basis of binary diffusion coefficients at infinite dilution of the implied components using the Darken [8], the Vignes [9], or another equations reviewed by Pertler *et al.* [10].

With respect to computer simulations, diffusivities, as well as other transport properties, can be calculated by the non-equilibrium simulations, or from the equilibrium correlation functions using the Green-Kubo formulas or the associated Einstein relations [2, 11].

Up till now it is not yet possible to provide a rigorous theoretical interpretation of diffusivities in dense fluids, because there are many-body interactions involved and the pair potential energy functions are only known for simple molecules [2]. Nevertheless, several models have been proposed in the literature for the calculation of diffusion coefficients in dense fluids, but they are usually applicable over restricted ranges of temperature and density, being in many cases specific for a particular physical state or inadequate to represent polar systems, particularly those with hydrogen-bounding solvents [1-2, 12]. Most of these approaches were described and reviewed by Reid *et al.* [12], Liong *et al.* [13], Millat *et al.* [1], Silva and Liu [2], and Medina [14].

Experimentally, the chromatographic peak broadening technique (CPB) has been widely used to measure D_{12} of solutes in pure or mixed solvents, which is based on the Taylor-Aris dispersion theory. The solvents commonly studied in the measurements are supercritical carbon dioxide (SC-CO_2) and liquid water. The data measured and published in the literature reflect their practical interest in specific applications. For instance, fatty acids, triacylglycerides, amino acids, sugars, and phenolic compounds have a significant relevance in food, pharmaceutical, and fuel industries [15-20]. Furthermore, it also worth mentioning organometallic compounds in SC-CO_2, as cobalt(III) acetylacetonate and palladium(II) acelylacetonane, which have been largely used in the preparation and processing of advanced functional materials, as catalysts or precursors [21-22], and like ferrocene and 1,1′-dimethylferrocene, since these compounds have a significant solubility in supercritical fluids and potential to control solvation and reaction behaviour through changes in the physical conditions of the system [23].

This thesis is aimed to install and test a new experimental unit to measure diffusion coefficients of solutes at infinite dilution in supercritical fluids and liquid mixtures, as well as to develop new models for D_{12}, applicable in gas and dense phases over wide ranges of temperature and density. A large database of experimental diffusivity values was collected and used to validate the new modes.

In the following, the structure of the present thesis is concisely presented. The document is divided into seven chapters.

In Chapter 2, an overview of the fundamental concepts for calculating binary diffusion coefficients at infinite dilution of model and real fluids is presented.

Chapter 3 contains the database collected in this work to validate the new models developed, and the properties used for all molecules involved in calculations (Chapter 4). This database is the largest ever compiled for this specific purpose, and comprehends extremely distinct molecules in terms of size, molecular weight, sphericity, and polarity.

In Chapter 4, all modelling results are listed, being directly based on eight international publications of the author (Papers I to VIII): *i*) Equations from Liu, Silva and Macedo, TLSM and TLSM_d, were revisited (Paper I) and tested with a much larger database; *ii*) A new equation for diffusion coefficients of the hard sphere system, F_{12}, established on molecular dynamics simulations (Paper II); *iii*) Two correlations applicable to non-polar or weakly polar solvents, with one parameter based on different fundamental frameworks to represent attractive contributions: Rice and Gray approach (Paper II) and an exponential activation energy (Paper III); *iv*) One D_{12} expression for polar systems (Paper IV), with two parameters that includes friction coefficients from the seminal Rice and Gray equation from which one is specific for polar interactions, namely based on the Stockmayer potential; *v*) A new free-volume correlation (Paper V) for supercritical carbon dioxide and liquid water that embodies simultaneously the concepts of free volume and activation energy; *vi*) A universal correlation based on Lennard-Jones model applicable to polar, non-polar, and weakly polar solvents (Paper VI). It contains two specific parameters, the solvent molecular diameter and the diffusion activation energy; *vii*) Empirical and semi-empirical 2-parameters equations dependent on temperature and/or solvent density and/or solvent viscosity (Paper VII); *viii*) Modified Stokes-Einstein equations to predict diffusivities in supercritical carbon dioxide (Paper VIII).

Chapter 5 provides a brief review of experimental methodologies to measure diffusivities. The chromatographic methods are described in more detail, since the experimental unit devised and installed in this work is of this type.

In Chapter 6, the experimental set-up, procedures, and tests are described in detail, as well as D_{12} measurements of acetone, toluene and eucalyptol in supercritical carbon dioxide using the chromatographic peak broadening (CPB) method. The assays were performed from 308.15 to 333.15K, and pressures from 150 to 252 bar. The influence of solvent density and viscosity are examined, and the data is modelled using the new models developed and studied in this work (Chapter 4).

Finally, the main and global conclusions of the thesis are compiled in Chapter 7.

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Part I
MODELLING

2. Theoretical Background

The transport of mass, momentum and energy through a fluid are phenomena that occur at microscopic level and are directly related with interactions between particles. Accordingly, the knowledge of their intermolecular potential presents in a fluid makes possible the estimation and calculation of all these properties. This chapter presents the theoretical fundamentals of diffusion phenomenon, in particular, first, pair potential functions frequently used in computer simulations are briefly described. Then, expressions and the main approaches for tracer diffusion coefficients derived of model and real fluids are presented.

2.1. Model Fluids: Intermolecular Potentials

The intermolecular potential, ϕ, allows the quantification of intermolecular forces (interactions between molecules), since it measures the required energy to bring together two molecules from infinite to a distance r. Commonly, this energy is a function of the separation and spatial orientation of the molecules involved. When they are non-polar spheres and, ϕ is only dependent on [1-2]. In this case, the intermolecular force, $F(r)$, can be obtained by the relation:

$$F(r) = -\frac{d\phi(r)}{dr} \tag{2.1}$$

From Eq. (2.1) it is possible to confirm that $\phi(r)$ corresponds to the work performed during the approximation of two molecules infinitely distant to a distance r:

$$\phi(r) = \int_r^\infty F(r)\, dr \tag{2.2}$$

In Figure 2.1 general representations of the potential energy and intermolecular force for a spherical molecule are presented. This specific potential is characterized by two parameters: the collision diameter, σ, which corresponds to the distance for which $\phi(r)=0$, and the maximum energy of attraction between the molecules, ε, which occurs at distance r_{m}, where the interaction forces are null, $F(r)=0$. When $r<r_{\mathrm{m}}$, the intermolecular forces are repulsive $(F(r)>0)$, while for values of $r>r_{\mathrm{m}}$ they are attractive $(F(r)<0)$. Frequently, the intermolecular potential is divided into three distinct regions where the type of interactions present can be: *i*) short-range, for $r<\sigma$, *ii*) medium-range, for $\sigma<r<2\,\sigma$, and *iii*) long-range, for $r>2\,\sigma$. The short-range forces are essentially repulsive, while the long-range are attractive [2].

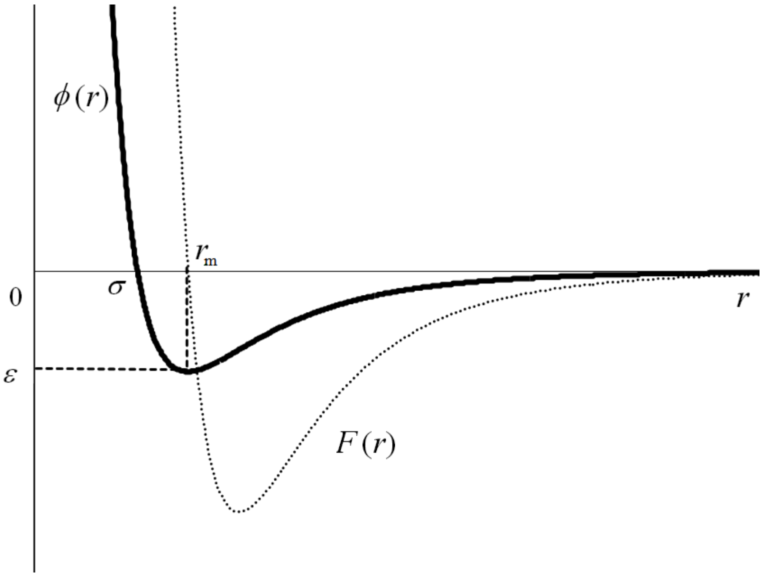

Figure 2.1. Generic representation of the intermolecular potential, $\phi(r)$, and its intermolecular force, $F(r)$, for a spherically symmetrical molecule.

In the following, well-known pair potentials that are frequently used in computer simulation studies of transport properties are briefly presented: hard sphere (HS), square-well (SW), soft sphere (SS), Lennard-Jones (LJ), repulsive Lennard-Jones (RLJ) or Week-Chandler-Andersen (WCA), and Stockmayer (ST).

2.1.1. Hard sphere potential

The hard sphere (HS) potential appeared as a first correction to the ideal gas, introducing a molecular excluded volume. This potential assumes that the molecules are rigid impenetrable spheres that cannot overlap in space, as “billiard” balls [1-3]:

$$\phi_{\mathrm{HS}}(r)=\begin{cases}\infty\,, & r\le\sigma\\ 0\,, & r>\sigma\end{cases} \tag{2.3}$$

where σ is the HS diameter. In Figure 2.2 a generic hard sphere potential is presented.

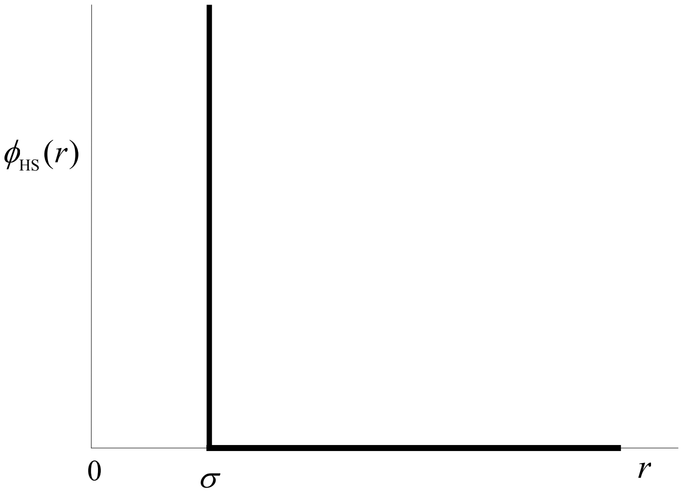

Figure 2.2. Hard sphere potential.

2.1.2. Square-well potential

This potential has the basic feature of a real fluid, since the presence of attractive and repulsive forces, in a crude fashion, are taken into account. In this model rigid spheres of diameter σ are surrounded by an attractive core of strength $\varepsilon_{\mathrm{SW}}$ which extends to separations $K\sigma$ (see Figure 2.3) [1-3]. In literature, the parameter K is often assumed to be 1.5.

$$\phi_{\mathrm{SW}}(r)=\begin{cases}\infty\,, & r\le\sigma\\ -\varepsilon_{\mathrm{SW}}\,, & \sigma<r<K\sigma\\ 0\,, & r\ge K\sigma\end{cases} \tag{2.4}$$

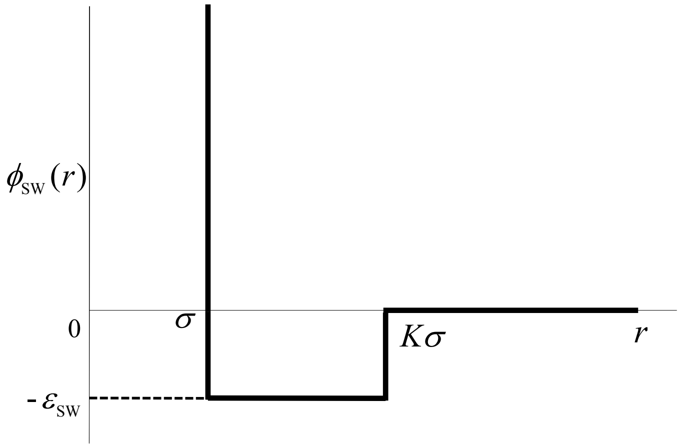

Figure 2.3. Square-well potential.

2.1.3. Soft spheres, Coulomb or one-component plasma potentials

The soft spheres (SS) are represented by a three-parameter potential that do not consider an attractive component, being commonly given by:

$$\phi_{\mathrm{SS}}(r) = \varepsilon(\sigma/r)^{\nu} \tag{2.5}$$

where ε is the energy parameter, σ is the collision diameter, and parameter ν characterizes the hardness of molecules. In the extreme case of $\nu = \infty$, it corresponds to the HS model, and if $\nu = 1$, the one-component plasma potential is recovered. Frequently, in literature the value of ν for SS fluid is 12 [3].

2.1.4. Lennard-Jones potential

Considering the previous models, the Lennard-Jones (LJ) model interprets more realistically the behaviour of a real fluid. It combines the inverse sixth power London forces with a very common repulsion term, $\phi_{\mathrm{rep}}(r) \propto r^{-12}$:

$$\phi_{\mathrm{LJ}}(r) = 4\,\varepsilon_{\mathrm{LJ}} \left[\left(\frac{\sigma_{\mathrm{LJ}}}{r} \right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r} \right)^{6} \right] \tag{2.6}$$

where $\varepsilon_{\mathrm{LJ}}$ is the depth of the potential well, which occurs at $r_{\mathrm{m}} = 2^{1/6}\sigma_{\mathrm{LJ}}$, corresponding to the point of maximum attraction, and σ_{LJ} is the collision diameter for the low energy collisions (the value of r for which $\phi_{\mathrm{LJ}}(r)=0$). These parameters, σ_{LJ} and $\varepsilon_{\mathrm{LJ}}$, are frequently called LJ parameters. In Figure 2.4 a generic LJ potential is shown [1-3].

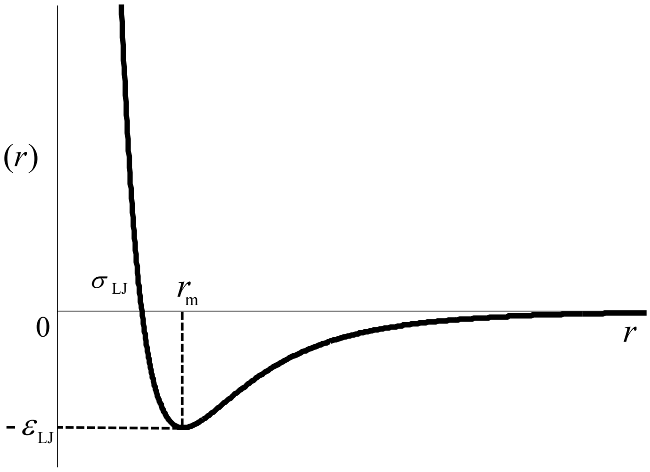

Figure 2.4. Pictorial representation of Lennar-Jones intermolecular potential.

2.1.5. *Repulsive Lennard-Jones or Week-Chandler-Andersen potential*

In 1971, Weeks *et al.* [4] divided up the LJ potential in two distinct terms: a reference that contains all repulsive contributions, and another one corresponding to a perturbation term, which comprises all attractive forces. Thus, the RLJ or WCA fluid is defined as

$$\phi_{\mathrm{WCA}}(r)=\begin{cases}\phi_{\mathrm{LJ}}(r)+\varepsilon_{\mathrm{LJ}}\ , & r \le 2^{1/6}\sigma_{\mathrm{LJ}} \\ 0\ , & r \ge 2^{1/6}\sigma_{\mathrm{LJ}}\end{cases} \tag{2.7}$$

2.1.6. *Stockmayer potential*

The previous potentials presented are able to predict the properties of non-polar fluids, while the Stockmayer (ST) fluid [5] has been widely used to interpret the behaviour of polar molecules. It is a combination of a LJ potential and the interactions of two point dipoles [1, 5]:

$$\phi_{\mathrm{LJ}}(r,\theta_{\mathrm{a}},\theta_{\mathrm{b}},\psi)=4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}-\xi\,\delta\left(\frac{\sigma}{r}\right)^{3}\right] \tag{2.8}$$

where

$$\xi = \frac{1}{2}\left(2\cos\theta_\mathrm{a}\cos\theta_\mathrm{b} - \sin\theta_\mathrm{a}\sin\theta_\mathrm{b}\cos\psi\right) \tag{2.9}$$

$$\delta = \frac{1}{2}\frac{\mu}{\varepsilon\sigma^2} \tag{2.10}$$

where θ_a and θ_b are the angles of inclination of the dipoles axes to the line joining the centres of the molecules, ψ is the azimuthal angle between them, and μ is the dipole moment. A comparison of ST potential for the pair separation of head-to-tail and head-to--head orientation with the LJ potential is shown in Figure 2.5:

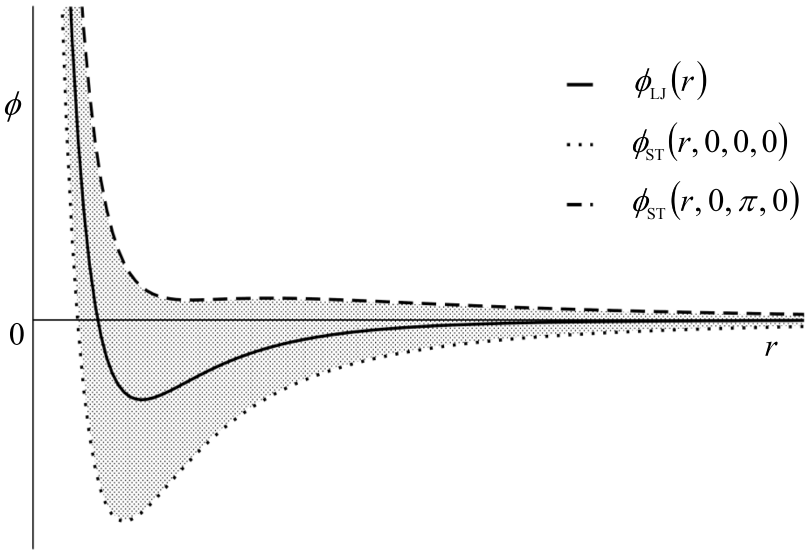

Figure 2.5. Comparison between the Lennard-Jones potential and the Stockmayer pair potential for dipole strength $\mu = 1$ at different orientation of the dipoles. In the shaded region the Stockmayer pair potential can adopt any intermediate value due to the orientation of the particles. Adapted from Bartke [6].

2.2. Diffusion Coefficients of Model and Real Fluids

The diffusion coefficients at infinite dilution, D_{12}, are key parameters for the design and scale-up of rate controlled separations and multiphase reactors. They are essential for concentrated solutions also, whether binary or multicomponent, where a Maxwell-Stefan (MS) approach is highly recommended. In fact, the necessary crossed MS diffusivities may be estimated from the binary ones at infinite dilution taking into account relations of the Vignes type [7].

Concerning modelling, several approaches for the calculation of diffusivities in dense fluids can be found in the literature, as for instance, kinetic theory, the free volume theory, hydrodynamic theory, the absolute-rate theory of Eyring, expressions based on idealized fluids (*e.g.*, hard sphere, square-well, Lennard-Jones, repulsive Lennard-Jones or Weeks-Chandler-Andersen), as well as for real fluids [3, 8-11]. In this section some theoretical foundations and their respective equations that allow the calculation of tracer diffusivities are presented.

2.2.1. Ideal gas

The diffusion coefficient of an infinitely diluted gas (*i.e.* in the limit of zero density), D_{12}^{0}, may be estimated from the kinetic theory of gases [3, 10]:

$$\rho_1^0 D_{12}^0 = \frac{3}{8\sigma_{12}^2}\left(\frac{k_\mathrm{B}\,T}{2\,\pi\,m_{12}}\right)^{1/2} \tag{2.11}$$

where superscript “0” stands for ideal gas, subscripts “1” and “2” denote solvent and solute, respectively, ρ is the number density, k_B is the Boltzmann constant, T is the absolute temperature, σ_{12} is the distance between the centres of the molecules at collision, and m_{12} is the reduced mass of the system. The values of σ_{12} and m_{12} are calculated from the individual molecular diameters and masses by:

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \tag{2.12}$$

$$m_{12} = \frac{m_1\,m_2}{m_1 + m_2} = \frac{1}{N_\mathrm{a}}\frac{M_1\,M_2}{\left(M_1 + M_2\right)} \tag{2.13}$$

Eq. (2.11) is valid for monoatomic gases, but in cases where molecules have internal structure, it should be modified. Furthermore, it is not applicable to dense fluids and liquids in view of the fact it is based on the Boltzmann equation for distribution function, which exclusively considers the occurrence of binary collisions, and assumes that the size of molecules are much smaller than their mean free path [3, 10].

2.2.2. Enskog fluid

In 1922, Enskog [3, 10, 12] developed a kinetic theory for transport properties of a dense HS systems, considering that the molecules diameters are not negligible, and modified the frequencies of collisions by the radial distribution function at contact point, $g(\sigma_{12})$. Thus, the system at high densities behaves like at low densities, being the unique difference the increase of collisions frequency. The Enskog equation for the tracer diffusion coefficient is related with the low density diffusivity, D_{12}^0, by:

$$\frac{\rho_1 D_{12,\mathrm{E}}}{\rho_1^0 D_{12}^0} = \frac{1}{g(\sigma_{12})} \tag{2.14}$$

The radial distribution function at contact, $g(\sigma_{12})$, can be calculated using different expressions. Mansoori *et al.* [13], from the solution of the Percus-Yevick integral equation for the mixture of hard spheres, proposed the following equation:

$$g(\sigma_{12}) = \frac{1}{(1-\varphi_1)^3}\left(1-\varphi_1+\frac{2\varphi_1}{1+\sigma_1/\sigma_2}\right)\left(1-\varphi_1+\frac{\varphi_1}{1+\sigma_1/\sigma_2}\right) \tag{2.15}$$

being φ_1 the solvent HS packing fraction, which for N_1 spheres that occupy a volume V_1 is given by:

$$\varphi_1 = \frac{N_1 \pi \sigma_1^3}{6V_1} = \frac{\pi}{6}\rho_1 \sigma_1^3 = \frac{\pi\sqrt{2}}{6}\left(\frac{V_{1,0}}{V_1}\right) = \frac{\pi}{6}\rho_1^* \tag{2.16}$$

where $V_{1,0} \equiv N_1\sigma_1^3/\sqrt{2}$ is the close-packed molar volume, and $\rho_1^* \equiv \rho_1 \sigma_1^3$ is the reduced number density of solvent. Another alternative to the previous equation is that of Carnahan and Starling [14]:

$$g(\sigma_{12}) = \frac{\sigma_1\, g(\sigma_2) + \sigma_2\, g(\sigma_1)}{\sigma_1 + \sigma_2} \tag{2.17}$$

being $g(\sigma_i)$ where $i = 1, 2$, given by

$$g(\sigma_i) = \frac{1}{1-\varphi} + \frac{3y_i}{2(1-\varphi)^2} + \frac{y_i^2}{2(1-\varphi)^3} \tag{2.18}$$

and

$$\varphi = \sum_i \varphi_i = \sum_i \pi\, \rho_i^* / 6 = \sum_i \pi\, \rho_i\, \sigma_i^3 / 6 \tag{2.19}$$

$$y_i = \frac{\sigma_i \varphi_j + \sigma_j \varphi_i}{\sigma_j} \quad , \quad \text{where} \quad i \neq j = 1, 2 \tag{2.20}$$

2.2.3. Hard sphere fluid

Enskog's equation is based on the molecular chaos approximation, and consequently it is not valid in a large density range, being its application very restricted. In 1974, Alder *et al.* [15], via computer simulations for HS systems of a single test particle in a solvent, for selected mass and size ratios, observed large deviations to the Enskog theory. The errors introduced neglecting correlated motions between core collisions gave raise to both backscattering and vortex flow effects, being necessary a correction. The first effect is more pronounced at high densities. In this process a sphere is closely surrounded by a shell of its neighbour spheres and blocked, and its velocity is reversed on collision, which leads to a decrease in diffusivities. At intermediate densities, persistence of unexpected velocities is responsible for an enhancement of the diffusion coefficient [3, 10, 16-17]. The HS tracer diffusivity of a solute through a solvent, $D_{12,\mathrm{HS}}$, is recurrently written as a modification of the Enskog value, by introducing a correction factor denoted by F_{12}:

$$D_{12,\mathrm{HS}} = \left(\frac{D_{12,\mathrm{HS}}}{D_{12,\mathrm{E}}} \right) D_{12,\mathrm{E}} \equiv F_{12}\, D_{12,\mathrm{E}} \tag{2.21}$$

The correction factor F_{12} depends on the solvent reduced number density, ρ_1^*, and on the size and mass ratios of both molecules:

$$F_{12} = F_{12}\left(\rho_1^*, \sigma_2/\sigma_1, m_2/m_1 \right) \tag{2.22}$$

The behavior of F_{12} is relatively complex as shown by the molecular dynamics (MD) data from Alder *et al.* [15]. In Figure 2.6 one may observed that for $\rho_1^* = 0.4714$, F_{12} increases with increasing σ_2/σ_1 for $m_2/m_1 = 1.00$, and at high densities, the correction factor always diminishes as σ_2/σ_1 increases.

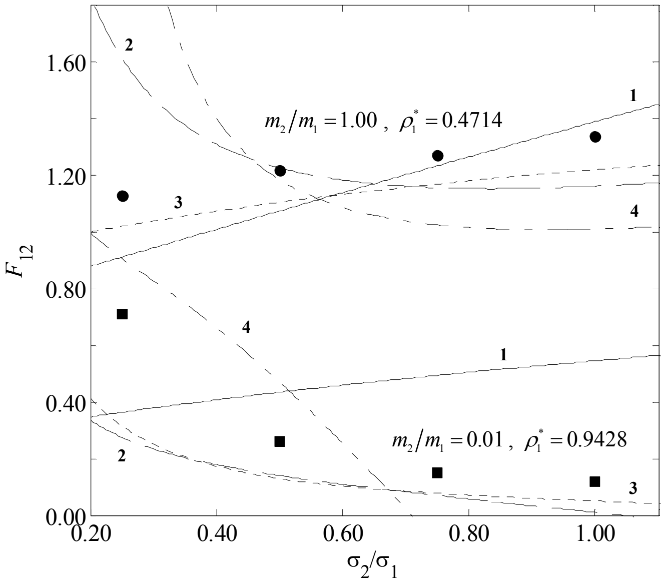

Figure 2.6. F_{12} correction factor for HS tracer diffusivities plotted against molecular size ratio. Legend: MD data of Alder *et al.* [15]: (●) $m_2/m_1 = 1.00$, $\rho_1^* = 0.4714$; (■) $m_2/m_1 = 0.01$, $\rho_1^* = 0.9428$; (1) Sung and Stell [18] (Eq. (2.27)); (2) Sun and Chen [19] (Eq. (2.32)); (3) Easteal and Woolf [20] (Eq. (2.33)); (4) Eaton and Akgerman [21] (Eq. (2.39)).

The correction factor, F_{12}, must satisfy the following four restrictions [3]:

a) For equal diameters and masses, F_{12} reduces to the self-diffusion correction factor, F_{11}, for which various good correlations are available in literature [22-25]:

$$\lim_{\substack{\sigma_2/\sigma_1 \to 1 \\ m_2/m_1 \to 1}} F_{12} = \frac{D_{11,\mathrm{HS}}}{D_{11,\mathrm{E}}} = F_{11}\left(\rho_1^*\right) \tag{2.23}$$

b) At low densities the Enskog diffusivity has to be recovered:

$$\lim_{\rho_1^* \to 0} F_{12}\left(\rho_1^*, \sigma_2/\sigma_1, m_2/m_1\right) = 1 \tag{2.24}$$

c) At low densities, the self-diffusion correction factor provided from Eq. (2.23), F_{11}, must satisfy the Enskog theory:

$$\lim_{\rho_1^* \to 0} F_{11}\left(\rho_1^*\right) = 1 \tag{2.25}$$

d) At an intrinsic high density, $\rho_s^* \approx 1.1$, the self-diffusion correction factor, F_{11}, should vanish, as indicate the MD simulations carried out by Woodcock [26]:

$$\lim_{\rho_1^* \to \rho_s^*} F_{11}\left(\rho_1^*\right) = 0$$

(2.26)

Some models have been proposed in literature for the hard sphere correction factor, F_{12}. In the following, those obtained by Sung and Stell [18], Sun and Chen [19], Easteal and Woolf [20], Eaton and Akgerman [21], and Liu and Ruckenstein [27] will be briefly described.

2.2.3.1. Sung and Stell model

Sung and Stell [18] derived analytically an expression for the correction factor F_{12}. The model can be considered as an improvement of the Enskog model at low densities and simultaneously embodies the correct hydrodynamic limit (Stokes-Einstein behaviour) at high density limit. As a result, their expression for the HS tracer diffusion coefficient may be written as follow:

$$F_{12} = \left(\frac{1 + \gamma_B \, \sigma_1/\sigma_2}{1 + \gamma \, \sigma_1/\sigma_2} \right)^2 \frac{g\left(\sigma_{12}\right)}{1 + 4\varphi_1 \, g\left(\sigma_{11}\right)} + \frac{1 + \sigma_1/\sigma_2}{1 + \gamma \, \sigma_1/\sigma_2} \, \frac{D_{12,\mathrm{H}}}{D_{12,\mathrm{E}}} \tag{2.27}$$

where γ and γ_B $\left(\gamma_B \equiv \lim_{\rho_1 \to 0} \gamma\right)$ are obtained numerically from the following relationship, which involves the Mansoori *et al.* [13] formula for $g\left(\sigma_{12}\right)$, and the Carnahan and Starling [28] equation of state for $g\left(\sigma_{11}\right)$:

$$\frac{1}{\left(1-\gamma^3\varphi_1\right)^3}\left(1-\gamma^3\varphi_1+\frac{2\gamma^3\varphi_1}{1+\sigma_1/\sigma_2}\right)\left(1-\gamma^3\varphi_1+\frac{\gamma^3\varphi_1}{1+\sigma_1/\sigma_2}\right)=1+4\varphi_1\frac{1-\varphi_1/2}{\left(1-\varphi_1\right)^3} \qquad (2.28)$$

The first term in the right hand side of Eq. (2.27) corresponds to the Enskog limit, while the second one is the hydrodynamic limit. The ratio $D_{12,\mathrm{H}}/D_{12,\mathrm{E}}$ is given by the Sun and Chen [29] equation:

$$\frac{D_{12,\mathrm{H}}}{D_{12,\mathrm{E}}}=2.881\left(1+\frac{\sigma_2}{\sigma_1}\right)\left(1+\frac{m_1}{m_2}\right)^{-1/2}\frac{\varphi_1\, g\left(\sigma_{12}\right)}{\eta_{1,\mathrm{HS}}/\eta_1^0} \qquad (2.29)$$

where $\eta_{1,\mathrm{HS}}/\eta_1^0$ is the ratio between the viscosities of the HS solvent and ideal gas. Taking into account the Enskog formula [3, 10] for viscosity, it is possible to write:

$$\frac{\eta_{1,\mathrm{HS}}}{\eta_1^0}=\left(\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}\right)\times\left(\frac{\eta_{1,\mathrm{E}}}{\eta_1^0}\right)=\left(\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}\right)\left[\frac{1}{g\left(\sigma_{11}\right)}+3.2\,\varphi_1+12.176\,\varphi_1^2 g\left(\sigma_{11}\right)\right] \qquad (2.30)$$

An accurate equation for $\eta_{1,\mathrm{HS}}/\eta_{1,\mathrm{E}}$ was obtained by Liu and Ruckenstein [27] using the MD simulations data from Alder *et al.* [16] for the HS fluid:

$$\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}=1+0.007825\,\rho_1^{*0.1}\exp\left(6.0037\,\rho_1^{*3}\right) \qquad (2.31)$$

2.2.3.2. Sun and Chen model

The Sun and Chen [19] empirical expression was supported by some data from Herman and Alder [30], Alder *et al.*[15] (data extrapolated to an infinite number of molecules, $N=\infty$), and Shelton [31], which cover the following ranges: $0.5<\sigma_2/\sigma_1<1.5$, $0.5<m_2/m_1<4.0$, and $1.5<V_1/V_{1,0}<3.0$. The parameters of the model were achieved by multiple regression:

$$F_{12}=1.0514\frac{\sigma_{12}^2}{\sigma_1\,\sigma_2}\left(\frac{2}{1+m_1/m_2}\right)^{1/2}\mathrm{g}\left(\sigma_{12}\right)\left(\frac{m_1}{m_2}\right)^{0.167}\left[1-0.9779\rho_1^*\left(\frac{m_1}{m_2}\right)^{0.0165}\left(\frac{\sigma_2}{\sigma_1}\right)^{0.129}\right] \qquad (2.32)$$

The radial distribution function at contact, $g(\sigma_{12})$, may be calculated by the Mansoori *et al.* [13] or the Carnahan and Starling [14] expressions (Eqs. (2.15) and (2.17), respectively).

2.2.3.3. Easteal and Woolf model

In 1990, Easteal and Woolf [20], based on their MD simulations for tracer diffusivities of HS systems, proposed an empirical model for the molecular-weight ratio (m_1/m_2) dependence of F_{12}/F_{11} involving three parameters (a_0, a_1 and a_2). Originally, these parameters were optimized for each value of density, what restricted the applicability of the equation. Afterwards, Salim and Trebble got round this problem and developed new generalized expressions for these parameters in terms of ρ_1^* and σ_2/σ_1:

$$\ln\left(\frac{F_{12}}{F_{11}}\times g^{-1}(\sigma_{12})\right)=a_0+a_1\ln\left(\frac{m_2}{m_1}\right)+a_2\ln^2\left(\frac{m_2}{m_1}\right) \tag{2.33}$$

$$a_0=-1.02564\,\rho_1^{*4}\ln\left(\frac{\sigma_2}{\sigma_1}\right) \tag{2.34}$$

$$a_1=-0.24107+1.27589h_{12}-1.35439h_{12}^2+0.62393h_{12}^3 \tag{2.35}$$

$$a_2=-0.056 \tag{2.36}$$

where $h_{12}=\rho_1^{*2}(\sigma_2/\sigma_1)$, and $g(\sigma_{12})$ can be calculated by the expressions derived from Mansoori *et al.* [13] or the Carnahan and Starling [14] (see Eqs. (2.15) and (2.17), respectively). For self-diffusion correction factor, F_{11}, Salim and Trebble [32] selected the model of Speedy [23], which from MD simulations of Alder *et al.* [15-16], Woodcock [26] (both results for a box system with N = 500 spheres), and Easteal *et al.* [33-34] (N = 432 spheres) provides:

$$F_{11}(\rho_1^*)=\left(1-\frac{\rho_1^*}{1.09}\right)\left[1+\rho_1^{*2}\left(0.4-0.83\rho_1^{*2}\right)\right]\times g(\sigma_{11}) \tag{2.37}$$

where the Carnahan and Starling [28] equation is used for the radial distribution function of the pure solvent, $g(\sigma_{11})$:

$$g(\sigma_{11}) = \frac{1-\varphi_1/2}{(1-\varphi_1)^3} \tag{2.38}$$

Nevertheless, it can be shown that when this model is applied for tracer diffusivities of HS systems *via* Eq. (2.33), it does not satisfy the low density restriction given by Eq. (2.24) due to Eqs. (2.35) and (2.36).

2.2.3.4. Eaton and Akgerman model

Eaton and Akgerman [21], based on smooth hard sphere model theory and MD simulations provided from Easteal and Woolf [20], proposed another expression for F_{12}:

$$F_{12} = a'\frac{V_{1,0}}{V_1}\left[\left(\frac{V_1}{V_{1,0}}\right)^{\alpha} - b_{12}\right] g(\sigma_{12}) \tag{2.39}$$

where

$$\alpha = \frac{\sigma_1}{\sigma_2} - \frac{1}{3} \tag{2.40}$$

$$b_{12} = \left(\frac{m_1}{m_2}\right)^{0.03587}\left[0.6001 + 0.8491\left(\frac{\sigma_1}{\sigma_2}\right) - 0.244\left(\frac{\sigma_1}{\sigma_2}\right)^2\right] \tag{2.41}$$

wherein α is dependent only upon the ratio σ_2/σ_1 (Eaton [35]), and $g(\sigma_{12})$ can be calculated from Eq. (2.15) or Eq. (2.17). Liu and Ruckenstein [27], using the same MD simulation data, obtained the following expression for the parameter a':

$$a' = 1.689\,(\sigma_2/\sigma_1)^{2.0674} \tag{2.42}$$

2.2.3.5. Liu and Ruckenstein model

In 1997, based on 53 MD simulation data points from Herman and Alder [30] and Alder *et al.* [15] (data extrapolated for $N = \infty$), Liu and Ruckenstein [27] published a new equation for F_{12}. They did not choose the MD data by Easteal and Woolf [20], because they were contradict by data from Alder *et al.* [16] and Erpenbeck and Wood [24]. Their empirical model was built in order to obey all restrictions given by Eqs. (2.23) – (2.26), and is valid in the following ranges: $0.0 \le \rho_1^* \le 0.9428$, $0.25 \le \sigma_2/\sigma_1 \le 1.00$, and $0.0002 \le m_2/m_1 \le 4.00$. The final expression is:

$$\frac{F_{12}}{F_{11}} = 1.0 + \sum_{i=1}^{10} b_i H_i \tag{2.43}$$

where coefficients b_i and functions H_i are listed in Table 2.1. The functions H_i are dependent on ρ_1^*, σ_2/σ_1, m_2/m_1, radial distribution functions at contact, $g(\sigma_{11})$ and $g(\sigma_{12})$ (computed by Carnahan and Starling [28] (Eq. (2.38)) and Mansoori *et al.* [13] (Eq. (2.15)), respectively), the ratio $\eta_{1,\mathrm{HS}}/\eta_1^0$ (derived theoretically by Sung and Stell [18], Eq. (2.30)), the ratio $\eta_{1,\mathrm{HS}}/\eta_{1,\mathrm{E}}$ determined from the MD simulation data of Alder *et al.* [16], Eq. (2.31), and the quantity Δ, which was obtained by Alder *et al.* [15] in order to take into account the hydrodynamic effects in F_{12}:

$$\Delta = \left[\frac{\eta_{1,\mathrm{HS}}/\eta_1^0 + 1.2/g(\sigma_{11})}{\eta_{1,\mathrm{HS}}/\eta_1^0 + 1.2(m_1/2m_{12})^{1/2}(\sigma_{11}/\sigma_{12})^2 g^{-1}(\sigma_{12})} \right]^{3/2} \tag{2.44}$$

Fitting MD data by Alder *et al.* [16], Erpenbeck and Wood [24] and Woodcock [26] for the pure HS fluid, Ruckenstein and Liu [22] attained a very accurate expression, in the whole density range ($0.0 < \rho_1^* < 1.08$), for F_{11}:

$$F_{11} = 1.0 + 0.94605\rho_1^{*1.5} + 1.4022\rho_1^{*3} - 5.6898\rho_1^{*5} + 2.6626\rho_1^{*7} \tag{2.45}$$

The model of Liu and Ruckenstein [27] has been reported in literature as the best F_{12} model with an average absolute relative deviation (AARD) equal to 4.97%, while the AARDs of Sun and Chen [19] and Sung and Stell [18] reach 34.51% and 75.62%, respectively. However, due to its complexity, even with current computing resources, its computational implementation is not attractive.

Table 2.1. Coefficients b_i and functions H_i for the F_{12} model of Liu and Ruckenstein [27] of tracer diffusion coefficients in a HS system (Eq. (2.43)).

i	b_i	H_i
1	-0.293977	$\chi \ln(\sigma_2/\sigma_1)$
2	-0.106089	$\chi \ln^2(\sigma_2/\sigma_1)\ln(m_2/m_1)$
3	0.111318	$\chi \ln(m_2/m_1)$
4	0.002865	$\ln(\eta_{1,\mathrm{HS}}/\eta_1^0)\ln^2(m_2/m_1)$
5	-0.0069724	$\chi \ln(m_2/m_1)(\sigma_1/\sigma_2)^{0.5}$
6	-0.0020652	$\chi \ln(\sigma_2/\sigma_1)(m_1/m_2)^{0.5}$
7	3.21576	$\ln^2[g(\sigma_{11})/g(\sigma_{12})]$
8	-0.334952	$\chi \ln \Delta$
9	-0.26190	$\chi \ln^2(\sigma_2/\sigma_1)(m_1/m_2)^{1/6}$
10	0.143989	$\delta(\sigma_2/\sigma_1, m_2/m_1)\ln(\eta_{1,\mathrm{HS}}/\eta_{1,\mathrm{E}})$

Note: $\chi = \rho_1^{*0.01}$; $\delta(\sigma_2/\sigma_1, m_2/m_1) = \begin{cases} 0, & \text{se } (\sigma_2/\sigma_1) \text{ e } (m_2/m_1) = 1.0 \\ 1, & \text{se } (\sigma_2/\sigma_1) \text{ ou } (m_2/m_1) \neq 1.0 \end{cases}$

In Figures 2.6 and 2.7, the models of Sung and Stell [18], Sun and Chen [19], Easteal and Woolf [20], and Eaton and Akgerman [21] are plotted together with MD data of Alder *et al.* [15], illustrating the dependence of F_{12} on σ_2/σ_1 and m_2/m_1, respectively. Taking into account the results of Figure 2.6, one concludes that the expressions of Sun and Chen [19] and Eaton and Akgerman [21], for $m_2/m_1 = 1.00$, $\rho_1^* = 0.4714$, do present noticeable wrong trends, since F_{12} decreases while data points increase. On the other hand, according to the theory of Sung and Steel [18], for $m_2/m_1 = 0.01$ and $\rho_1^* = 0.9428$, F_{12} increases whereas MD data decrease. From Figure 2.7, it is possible to verify that Sun and Chen [19] model always underestimates F_{12}, and that Eaton and Akgerman [21] equation overestimates it at low values of m_2/m_1 and underestimates at high values of m_2/m_1. In general, all models from literature describe deficiently the behaviour of this correction factor.

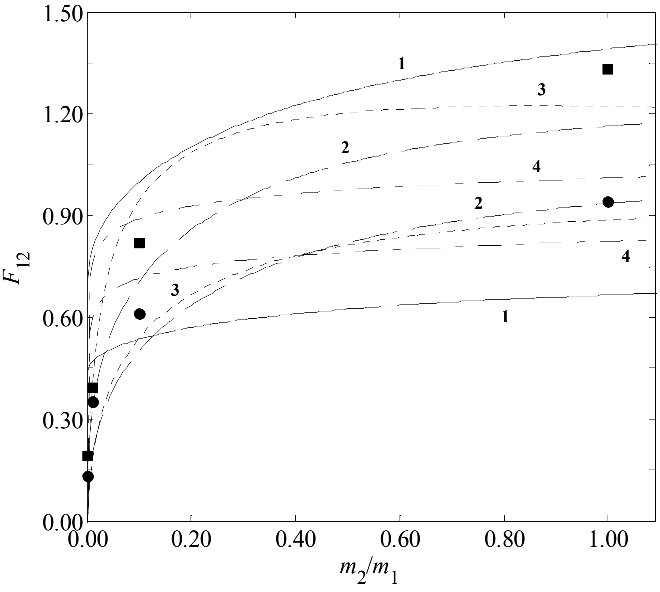

Figure 2.7. Correction factor for the tracer diffusion coefficient of HS system *versus* molecular weight ratio. Legend: MD data of Alder *et al.* [15]: (■) $\sigma_2/\sigma_1 = 1.00$, $\rho_1^* = 0.4714$; (●) $\sigma_2/\sigma_1 = 0.50$, $\rho_1^* = 0.8839$; (1) Sung and Stell [18] (Eq. (2.27)); (2) Sun and Chen [19] (Eq. (2.32)); (3) Easteal and Woolf [20] (Eq. (2.33)); (4) Eaton and Akgerman [21] (Eq. (2.39)).

2.2.4. Lennard-Jones fluid

The tracer diffusion coefficient of a LJ fluid can be achieved by substituting an effective diameter on the HS model and by coupling an attractive contribution. This may be performed in two different ways: by the Rice and Gray approach [3, 22, 27, 36], and by multiplying activation expressions like Straub [37] and Speedy *et al.* [38] did. A description of these aspects is presented in the following subsections.

2.2.4.1. Effective hard sphere diameters

The effective hard sphere diameter (EHSD) method has been widely used in calculations of both transport and thermodynamic properties. The main underlying assumption of this method is that a property of a fluid can be calculated from a HS model if the molecular diameter is replaced by an EHSD, σ_{eff}. Thus, a transport property Y can be generically represented by

$$Y\left(T^*, \rho^*\right) = Y_{\text{HS}}\left[\rho^*, \sigma_{\text{eff}}\left(T^*, \rho^*\right)\right] \tag{2.46}$$

where $T^* = T/(\varepsilon/k_B)$ and ρ^* are the reduced temperature and density, respectively [3].

Several expressions for EHSD have been proposed in literature. Some of them are purely empirical (*e.g.* Heyes [39-40], Hammonds and Heyes [41], Sun *et al.* [42]), while others were designed according to certain criteria, namely, Boltzmann [3, 43], Barker-Henderson [44], Weeks-Chandler-Andersen (WCA) [4, 45], and Lado [46]. The theoretical formulation of these criteria are clearly explained in Silva *et al.* [43], and Silva and Liu [3]. Silva *et al.* [43] carried out a comparison between fifteen models and applied them to predict LJ self-diffusivities using the Erpenbeck and Wood [24] model for HS fluid. The best results were attained by temperature-dependent Boltzmann EHSDs, *e.g.* Ben-Amotz and Herschbach (BAH) [47], derived from the equilibrium data, and Liu *et al.* (BLSM) [25] expressions:

$$\sigma_{\mathrm{BAH}}\left(T^*\right) = 1.1532\,\sigma_{\mathrm{LJ}}\left[1 + \left(1.8975\,T^*\right)^{\frac{1}{2}}\right]^{-\frac{1}{6}} \tag{2.47}$$

$$\sigma_{\mathrm{BLSM}}\left(T^*\right) = 2^{\frac{1}{6}}\,\sigma_{\mathrm{LJ}}\left[1 + \left(1.3229\,T^*\right)^{\frac{1}{2}}\right]^{-\frac{1}{6}} \tag{2.48}$$

as well as by the temperature- and density-dependence Lado modified WCA EHSD, namely the equation obtained by Ben-Amotz and Herschbach (LWCAAH) [47]:

$$\sigma_{\mathrm{LWCAAH}}\left(T^*, \rho^*\right) = 1.1137\,\sigma_{\mathrm{LJ}}\left[1 + \left(\frac{T^*}{T_0^*}\right)^{\frac{1}{2}}\right]^{-\frac{1}{6}} \tag{2.49}$$

where

$$\left(T_0^*\right)^{-\frac{1}{2}} = 0.72157 + 0.04561\rho^* - 0.07468\rho^{*2} + 0.12344\rho^{*3} \tag{2.50}$$

2.2.4.2. Attractive Contribution

According to Kushick and Berne [48] and Straub [37], the attractive forces play an important role in transport properties, especially at low temperature. The introduction of the attractive contribution can be carried out using two different approaches:

i) Rice and Gray approach [36]: According to these authors, the diffusion coefficient of the LJ fluid, can be generally calculated as:

$$D_{\mathrm{LJ}} = \frac{k_{\mathrm{B}} T}{\zeta_{\mathrm{R}} + \zeta_{\mathrm{S}}} \tag{2.51}$$

where ζ_{R} is the repulsive friction coefficient, and ζ_{S} is a soft attraction friction coefficient. When $\zeta_{\mathrm{S}} = 0$, the expression for a HS fluid is recovered (Eq. (2.21)). Thus, the equation for a LJ fluid can be obtained by adding an attractive term, ζ_{S}, to the repulsive one, ζ_{R}, and replacing the molecular diameter by an EHSD dependent on the temperature and/or density [3, 22, 27]. In 1997, Ruckenstein and Liu [22] applied successfully this approach to calculate LJ self-diffusivities, and, later on, the same authors extended their expression for binary systems at infinite dilution [27]:

$$D_{12,\mathrm{LJ}} = \frac{k_{\mathrm{B}} T}{\zeta_{12,\mathrm{R}} + \zeta_{12,\mathrm{S}}} \tag{2.52}$$

where from Eqs. (2.14) and (2.21) it is clear that:

$$\zeta_{12,\mathrm{R}} = \frac{8}{3} \rho_1 \sigma_{12,\mathrm{eff}}^2 \sqrt{2 \pi m_{12} k_{\mathrm{B}} T} \frac{g(\sigma_{12,\mathrm{eff}})}{F_{12}} \tag{2.53}$$

With regard to $\zeta_{12,\mathrm{S}}$, Ruckenstein and Liu [22] derived the following equation:

$$\zeta_{12,S} = \frac{8}{3} \rho_1 \sigma_{12,\mathrm{eff}}^2 \sqrt{2 \pi m_{12} k_{\mathrm{B}} T} \frac{0.4}{T_{12}^{*1.5}} \tag{2.54}$$

When Eqs. (2.53) and (2.54) are substituted in Eq. (2.52), the model for $D_{12,\mathrm{LJ}}$ is found:

$$D_{12,\mathrm{LJ}} = \frac{k_{\mathrm{B}} T}{\frac{8}{3} \rho_1 \sigma_{12,\mathrm{eff}}^2 (2 \pi m_{12} k_{\mathrm{B}} T)^{1/2} \left[\frac{g(\sigma_{12,\mathrm{eff}})}{F_{12}} + \frac{0.4}{T_{12}^{*1.5}} \right]} \tag{2.55}$$

The effective diameter of the system, $\sigma_{12,\mathrm{eff}}$, is computed by the expression of Ben-Amotz and Herschbach [47] according to Boltzmann criterion (Eq. (2.47)), the radial distribution function at contact $g(\sigma_{12,\mathrm{eff}})$ is calculated by the Carnahan and Starling [14] equation (Eq.(2.17)), and the correction factor F_{12} is given by Liu and Ruckenstein [27] model (Eq. (2.43)). Both calculations of $g(\sigma_{12,\mathrm{eff}})$ and F_{12} involve HS effective diameters, $\sigma_{1,\mathrm{eff}}$ and $\sigma_{2,\mathrm{eff}}$, which are determined by Eq. (2.47). The implied reduced temperatures are:

$$T_i^* \equiv \frac{k_\mathrm{B} T}{\varepsilon_{i,\mathrm{LJ}}} \qquad i = 1, 2, 12 \tag{2.56}$$

and the binary LJ force constants are evaluated by the classical Lorentz-Berthlot combining rules:

$$\sigma_{12,\mathrm{LJ}} = \frac{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}{2} \tag{2.57}$$

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right) \times \left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)} \tag{2.58}$$

where the individual LJ parameters are estimated as functions of critical temperature and molar volume of each compound by:

$$\sigma_{i,\mathrm{LJ}}(\text{Å}) = 0.7889\, V_{\mathrm{c},i}^{1/3} \tag{2.59}$$

$$\frac{\varepsilon_{i,\mathrm{LJ}}}{k_\mathrm{B}}(\mathrm{K}) = \frac{T_{\mathrm{c},i}}{1.2593} \tag{2.60}$$

Eq. (2.59) was derived from self-diffusion coefficient data [22], and Eq. (2.60) was obtained from viscosity data [9]. In previous equations, $V_{\mathrm{c},i}$ and $T_{\mathrm{c},i}$ are expressed in $\mathrm{cm^3 \cdot mol^{-1}}$, and K, respectively.

ii) Kushick and Berne [48], and Straub [37] approach: These authors showed that at low temperature it is necessary to take into account the differences between repulsive LJ (WCA) and LJ fluids. The LJ fluid expression is assembled as follows:

a) First, the EHSD method is applied to the HS fluid, giving rise to a model for WCA fluid, since the repulsive interactions play a dominant role between molecules [25]:

$$D_{\mathrm{WCA}}\left(T^*,\rho^*\right)=D_{\mathrm{HS}}\left[\rho^*,\sigma_{\mathrm{eff}}\left(T^*,\rho^*\right)\right] \tag{2.61}$$

b) Secondly, the LJ model is obtained as a perturbation on the WCA fluid, by introducing an exponential term to express the attractive contribution. Thus, both diffusivities, D_{WCA} and D_{LJ}, are related by means of simple temperature-dependent expressions and involve one parameter that can be optimized from MD data:

$$D_{\mathrm{LJ}}=D_{\mathrm{WCA}}\times f\left(\alpha_{\mathrm{LJ}}/T^*\right) \tag{2.62}$$

where α_{LJ} is the adjustable parameter. Several equations have been proposed in literature to express the attractive contributions, like those of Straub [37] and Speedy *et al.* [38].

Following this procedure, Speedy *et al.* [38] proposed for the LJ diffusivities the Eq. (2.62) with $\alpha_{\mathrm{LJ}}=0.5$ (parameter fitted from MD data):

$$D_{\mathrm{LJ}}=D_{\mathrm{HS}}\left(\rho^*,\sigma_{\mathrm{eff}}\right)\,\exp\left(-\frac{\alpha_{\mathrm{LJ}}}{T^*}\right) \tag{2.63}$$

Liu *et al.* [25], adopting the same approach published a new expression for the LJ self-diffusivities and extended it to binary diffusion coefficients at infinite dilution, $D_{12,\mathrm{TLSM}}$ [49] :

$$D_{12,\mathrm{TLSM}}=\frac{21.16}{\rho_1\sigma_{12,\mathrm{eff}}^2}\left(\frac{1000\Re_{\mathrm{g}}T}{2M_{12}}\right)^{1/2}\exp\left(-\frac{0.75\rho_1^*}{1.2588-\rho_1^*}-\frac{0.27862}{T_{12}^*}\right) \tag{2.64}$$

$\Re_{\mathrm{g}}=8.3144\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ is the universal gas constant; the effective diameters ($\sigma_{12,\mathrm{eff}}$, $\sigma_{1,\mathrm{eff}}$ and $\sigma_{2,\mathrm{eff}}$) are calculated by Eq. (2.48), ρ_1^* by Eq. (2.16), $M_{12}=M_1M_2/\left(M_1+M_2\right)$, and T_{12}^* by Eq. (2.56). The binary LJ diameter, $\sigma_{12,\mathrm{LJ}}$, is computed by Eq. (2.57), and the binary LJ energy, $\varepsilon_{12,\mathrm{LJ}}$, is given by the following combining rule proposed by Liu *et al.* [49]:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_{\mathrm{B}}}=\frac{\sqrt{\sigma_{1,\mathrm{LJ}}^{3}\left(\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}\right)\times\sigma_{2,\mathrm{LJ}}^{3}\left(\varepsilon_{2,\mathrm{LJ}}/k_{\mathrm{B}}\right)}}{\sigma_{12,\mathrm{LJ}}^{3}} \tag{2.65}$$

The individual LJ force constants are calculated by the corresponding states correlations (with critical constants in K and bar) [50]:

$$\frac{\varepsilon_{i,\mathrm{LJ}}}{k_{\mathrm{B}}}(\mathrm{K})=0.774\,T_{\mathrm{c},i} \tag{2.66}$$

$$\sigma_{i,\mathrm{LJ}}^{3}\left(\mathrm{\mathring{A}}^{3}\right)=0.17791+11.779\left(\frac{T_{\mathrm{c},i}}{P_{\mathrm{c},i}}\right)-0.049029\left(\frac{T_{\mathrm{c},i}}{P_{\mathrm{c},i}}\right)^{2} \tag{2.67}$$

This predictive model of Liu, Silva and Macedo (Eqs. (2.64) + (2.57) and (2.65)) leads to a global AARD = 14.77 % for 77 systems containing 1033 experimental data under liquid, gaseous and supercritical conditions.

In 2002, Zhu *et al.* [51] developed another model for the LJ system, with the ultimate goal of extending it to the real fluids. This model is based on the HS expression of Speedy [23], where eight parameters were fitted, and an exponential attractive contribution was incorporated:

$$\begin{aligned}D_{12,\mathrm{Zhu}}&=\frac{3}{8\sqrt{\pi}}\sqrt{\frac{\sigma_{12,\mathrm{LJ}}^{2}\;\varepsilon_{12,\mathrm{LJ}}}{m_{1}}}\,\frac{\sqrt{T_{12}^{*}}}{\rho_{12}^{*}}\left(1-\frac{\rho_{12}^{*}}{1.029079\;T_{12}^{*\,0.165377}}\right)\\&\times\left[1+\rho_{12}^{*\,0.126978}\left(\frac{0.596103\left(\rho_{12}^{*}-1\right)}{0.539292\left(\rho_{12}^{*}-1\right)+T_{12}^{*\left(0.400152-0.41054\,\rho_{12}^{*}\right)}}+0.68856\right)\right]\\&\times\exp\left(-\frac{\rho_{12}^{*}}{2\,T_{12}^{*}}\right)\end{aligned} \tag{2.68}$$

Here, T_{12}^{*} is calculated by Eq. (2.56), but distinct reduced density is introduced, as $\sigma_{12,\mathrm{LJ}}$ is implied instead of $\sigma_{2,\mathrm{LJ}}$:

$$\rho_{12}^{*} = \rho_1 \, \sigma_{12,\mathrm{LJ}}^{3} \tag{2.69}$$

The combining rule adopted for LJ diameter was derived by Zhu *et al.*[52]:

$$\sigma_{12,\mathrm{LJ}} = \frac{3}{4}\sigma_{1,\mathrm{LJ}} + \frac{1}{4}\sigma_{2,\mathrm{LJ}} \tag{2.70}$$

while the binary LJ energy is assessed by the classical rule (Eq. (2.58)). The individual LJ force constants of solvent and solute are estimated by distinct expressions:

$$\frac{\varepsilon_{1,\mathrm{LJ}}}{k_\mathrm{B}}(\mathrm{K}) = \frac{T_{\mathrm{c},1}}{T_{\mathrm{c},1}^{*}}\left[1 + 0.47527332\rho_{\mathrm{r},1} + \left(0.06300484 + 0.12374707\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{2.71}$$

$$\sigma_{1,\mathrm{LJ}}(\mathrm{cm}) = \left(\frac{\rho_{\mathrm{c},1}^{*}}{\rho_{\mathrm{c},1}}\right)^{1/3}\left[1 - 0.0368868\,\rho_{\mathrm{r},1} + \left(0.00006945 + 0.01089228\,\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{2.72}$$

$$\frac{\varepsilon_{2,\mathrm{LJ}}}{k_\mathrm{B}} = \frac{T_{\mathrm{c},2}}{1.313} \tag{2.73}$$

$$\sigma_{2,\mathrm{LJ}} = \sqrt[3]{\frac{0.13\,\varepsilon_{2,\mathrm{LJ}}}{P_{\mathrm{c},2}}} \tag{2.74}$$

The previous equations are based on the principle of corresponding states and on the critical point computed by Johnson *et al.* [53] for the LJ fluid ($P_\mathrm{c}^{*} = 0.13$, $T_\mathrm{c}^{*} = 1.313$ and $\rho_\mathrm{c}^{*} = 0.31$).

Note that the LJ models described above were firstly designed for self-diffusion coefficients and have been extended to binary diffusivities after some modifications.

2.2.5. Real fluid

The calculation of tracer diffusion coefficients in a real system can be performed by different approaches. In this section the most important theories and equations that are available in literature will be presented, namely, molecularly base models, free-volume theory, hydrodynamic models, and empirical/semi-empirical expressions.

2.2.5.1. Molecularly base models

As previously mentioned, the LJ fluid is a model fluid that takes into account both interaction contributions, repulsive and attractive. For this reason, it is usual the development of expressions for the diffusivity of real systems from LJ equations, by the introduction of one or more parameters to fit their real behaviour as accurately as possible [3]. The equations presented above for the LJ fluid – Liu and Ruckenstein [27], Liu, Silva and Macedo [49], and Zhu *et al.* [51] models – were extended to real fluids and validated using data for gas, liquid and supercritical states, and for non-polar or weakly polar solvents. They will be briefly described in the following.

2.2.5.1.1. Liu and Ruckenstein model

In order to take into consideration the polyatomic or non-spherical nature of real molecules, Liu and Ruckenstein multiplied Eq. (2.55) by a roughness factor, A_D [27]. This parameter takes into account the exchange of angular and linear momentum of molecules during an instantaneous collision [3, 54]. As Chandler [54], they assumed that A_D is independent of temperature and density, although some studies have been shown it can be a function of both variables [55]. Furthermore, the correction factor F_{12} derived by these authors (Eq. (2.43)) is limited to ranges of molecular size and mass ratios: $0.25 \le \sigma_2/\sigma_1 \le 1.00$, and $0.0002 \le m_2/m_1 \le 4.00$. In order to extend the applicability of their LJ model (Eq. (2.55)) to real systems, they introduced an empirical factor which was determined by experimental data:

$$D_{12,\,\mathrm{TLR}} = A_\mathrm{D}\left(\frac{\sigma_{2,\mathrm{LJ}}}{\sigma_{1,\mathrm{LJ}}}\right)^{0.42}\left(\frac{m_2}{m_1}\right)^{0.06} D_{12,\mathrm{LJ}} \tag{2.75}$$

From the relation between LJ diameter and critical volume (Eq. (2.59)), the previous equation can be written as:

$$D_{12,\mathrm{TLR}} = A_\mathrm{D}\left(\frac{V_{\mathrm{c},2}}{V_{\mathrm{c},1}}\right)^{0.14}\left(\frac{m_2}{m_1}\right)^{0.06} D_{12,\mathrm{LJ}} \tag{2.76}$$

Combining Eqs. (2.55) and (2.76), the final expression for tracer diffusivities proposed by Liu and Ruckenstein [27], $D_{12,\mathrm{TLR}}$, is obtained:

$$D_{12,\mathrm{TLR}} = \frac{A_\mathrm{D}\left(V_{\mathrm{c},2}/V_{\mathrm{c},1}\right)^{0.14}\left(m_2/m_1\right)^{0.06} k_\mathrm{B}\, T}{\frac{8}{3}\rho_1 \sigma_{12,\mathrm{eff}}^2 \left(2\pi m_{12} k_\mathrm{B}\, T\right)^{1/2}\left[\frac{g(\sigma_{12,\mathrm{eff}})}{F_{12}} + \frac{0.4}{T_{12}^{*1.5}}\right]} \tag{2.77}$$

where A_D is an adjustable parameter of each binary system.

In order to make their model purely predictive, these authors used Eqs. (2.59) and (2.60) to calculate the LJ parameters of each component, and correlated the coupling factor, A_D, with the binary acentric factor, ω_{12} [27]:

$$A_\mathrm{D} = 1 - 0.0133\,\omega_{12} - 0.3662\,\omega_{12}^2 \tag{2.78}$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{2.79}$$

This predictive model, TLR, was validated with 1443 data points for 120 systems, covering gas, liquid and supercritical systems, giving rise to an AARD of 8.42%. When the roughness factor, A_D, is taken as an adjustable parameter specific of each pair of components, a 1-parameter correlation denoted by $\mathrm{TLR}_{A_\mathrm{D}}$ is obtained. The global AARD found, in this case, is 5.10%. Nonetheless, Eq. (2.77) should not be applied to hydrogen-bonding systems [3, 27].

These correlation and predictive models are not considered for comparison in this thesis due to the impossibility to reproduce the values of F_{12}. The original paper must have an error but the authors were not able to clarify the problem.

2.2.5.1.2. *Liu-Silva-Macedo model*

Liu, Silva and Macedo [49] derived an expression for $D_{12,\mathrm{LJ}}$, denoted by $D_{12,\mathrm{TLSM}}$ (Eq. (2.64)), and from which two 1-parameter correlations were developed, by inserting interaction parameters, $k_{12,\mathrm{en}}$ and $k_{12,\mathrm{d}}$, into diameter and energy combining rules, respectively. In the correlation that contains the interaction energy parameter ($\mathrm{TLSM}_{\mathrm{en}}$), the combining rule for $\varepsilon_{12}/k_\mathrm{B}$ is expressed as:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \left(1-k_{12,\mathrm{en}}\right)\frac{\sqrt{\sigma_{1,\mathrm{LJ}}^3\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right)\times\sigma_{2,\mathrm{LJ}}^3\left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)}}{\sigma_{12,\mathrm{LJ}}^3} \tag{2.80}$$

where $k_{12,\mathrm{en}}$ is an adjustable parameter, and $\sigma_{12,\mathrm{LJ}}$ is calculated by Eq. (2.57). In the case of the correlation with an interaction diameter parameter (TLSM_d), the combining rule for $\sigma_{12,\mathrm{LJ}}$ is:

$$\sigma_{12,\mathrm{LJ}} = \left(1-k_{12,\mathrm{d}}\right)\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \tag{2.81}$$

where $k_{12,\mathrm{d}}$ is the adjustable parameter, and $\varepsilon_{12}/k_\mathrm{B}$ is computed by:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = 8\frac{\sqrt{\sigma_{1,\mathrm{LJ}}^3\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right)\times\sigma_{2,\mathrm{LJ}}^3\left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)}}{\left(\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}\right)^3} \tag{2.82}$$

Both correlations, $\mathrm{TLSM}_{\mathrm{en}}$ and TLSM_d, were tested with the same database of TLSM model (Eqs. (2.64) + (2.57) and (2.65)), totalizing 77 systems and 1033 experimental data, and very similar results were achieved between them, 6.50% and 6.57%, respectively. It is shown in Paper I (Chapter 4) that good results were also achieved when TLSM_d expression was tested with a much larger database (296 systems and 5279 data points).

2.2.5.1.3. Model of Zhu et al.

In order to predict tracer diffusivities of real systems, Zhu *et al.* [51] introduced an interaction parameter, k_{12}^d, using a combining rule adopted for the LJ diameter of the system, $\sigma_{12,\mathrm{LJ}}$:

$$\sigma_{12,\mathrm{LJ}} = \left(1-k_{12}^\mathrm{d}\right)\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \tag{2.83}$$

where

$$k_{12}^{\mathrm{d}} = 0.7926\,\frac{\sigma_{2,\mathrm{LJ}} - \sigma_{1,\mathrm{LJ}}}{\sigma_{2,\mathrm{LJ}} + \sigma_{1,\mathrm{LJ}}} \tag{2.84}$$

The predictive model has been tested with 74 systems containing 1141 experimental data, giving rise to AARD = 17.32%.

2.2.5.2. Free-volume theories

The free-volume theories are an alternative to determine transport properties of dense fluids, with special emphasis for liquids. It is assumed that the related coefficients (D, η, and λ: diffusion coefficient, viscosity, and thermal conductivity, respectively) are dependent on the relative expansion from an intrinsic molar volume, V_{i}, which is denoted by free volume: $V_{\mathrm{f}} = V - V_{\mathrm{i}}$. These theories have had a significant importance due to the following reasons: *i*) their equations are simple and a low number of parameters are employed (frequently between two and four); *ii*) the parameters, almost always, possess a physical meaning; *iii*) they can be used in vast ranges of temperature and pressure; *iv*) they are supported by the statistical mechanics, which gives them a significant consistency; and *v*) they can be extended to multicomponent systems [3, 56].

The free-volume models can be divided into two main groups. The first one relates the transport coefficients just with molar free volume, V_{f}:

$$D, \eta^{-1}, \lambda^{-1} = f\left(V_{\mathrm{f}}\right) \tag{2.85}$$

This type of equations is valid for fluids without attractive interactions. The second group comprises hybrid models that combine the concepts of free volume and activation energy, E_{a}, where both repulsive and attractive interactions are taken into account:

$$D, \eta^{-1}, \lambda^{-1} = f\left(V_{\mathrm{f}}\right)\exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \tag{2.86}$$

2.2.5.2.1. *Dymond free-volume expression*

A well-known example of a model based on the free-volume theory is the Dymond's expression, originally developed for self-diffusion of hard spheres [57] and later extended to binary systems (Chen *et al.*[58]):

$$D_{12,\mathrm{Dym}} = B\sqrt{T}\left(V_1 - V_\mathrm{D}\right) \tag{2.87}$$

This model embodies two adjustable parameters: B is a constant characteristic of the solvent-solute pair, and V_D is a constant related primarily with the solvent. It has been reported in literature that this equation leads to two physically meaningless results: quite different values of V_D's for the same solvent, and even negative values. In addition, this model should be used only for interpolation, a fact that limits its application outside the fitting interval [49].

2.2.5.2.2. *He-Yu-Su model*

These authors [59], based on free-volume type models, developed an expression to estimate the tracer diffusion coefficients of liquid and solid solutes in supercritical solvents:

$$D_{12,\mathrm{HYS}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right) = A\times10^{-7}\left(V_1^k - B'\right)T\big/\sqrt{M_2} \tag{2.88}$$

where

$$\begin{aligned} &k = 1, \quad \rho_{\mathrm{r},1} \geq 1.2 \\ &k = 1 + \left(\rho_{\mathrm{r},1} - 1.2\right)\big/\sqrt{M_1}, \quad \rho_{\mathrm{r},1} < 1.2 \end{aligned} \tag{2.89}$$

V_1 is the solvent volume ($\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$), $\rho_{\mathrm{r},1}$ is the reduced density of the solvent computed with its critical density. The parameters A and B' were fitted using experimental data (105 binary systems/1146 data points) and are dependent on the solvent properties (molecular weight, and critical volume, pressure and temperature):

$$\begin{aligned} &A = 0.29263 + 1.6736\times\exp\left(-0.75832\,\frac{\sqrt{M_1 V_{\mathrm{c},1}}}{P_{\mathrm{c},1}}\right), \quad \rho_{\mathrm{r},1} \geq 0.21 \\ &B' = 0.077\,T_{\mathrm{c},1}, \quad \rho_{\mathrm{r},1} \geq 0.21 \end{aligned} \tag{2.90}$$

2.2.5.3. Hydrodynamic models

In addition to the aforementioned models, there are numerous expressions based on the hydrodynamic theory, which comprise good alternatives, since they are simple, involve a small set of input data, and are frequently predictive. The hydrodynamic approach to mass transport is based on the Stokes-Einstein expression which establishes that the diffusivity of a solute through a solvent is directly proportional to the absolute temperature, T, and inversely proportional to the solvent viscosity, η_1:

$$D_{12} = \frac{k_{\mathrm{B}}\,T}{6\eta_1\,\pi\,r_2} \tag{2.91}$$

where r_2 is the radius of the solute molecule. The Stokes-Einstein model was firstly derived assuming that a large rigid spherical molecule of solute is moving through a continuum of solvent ($r_1 << r_2$) under infinitely dilute conditions, where the system is considered an ideal mixture [60]. Several well-known models in literature follow this pure ($D_{12} \propto T/\eta_1$) or modified dependence as, for instance, Wilke-Chang [9, 11, 61], Tyn--Calus [9, 62], Scheibel [11, 63], Reddy-Dorawasmy [11, 64], Lusis-Ratcliff [11, 65], and Lai-Tan [66] equations (see Table 2.2, Eqs. (2.92) to (2.99)). These models were originally developed for liquid systems but are commonly extended to supercritical fluids [11, 67], with exception to the Lai-Tan [66] equation that was designed and validated only for supercritical carbon dioxide systems. Nonetheless, this approach has been shown to fail in the supercritical region at lower densities attributed to the significant amount of clustering around the solutes, which results in an overestimation of the diffusion coefficients [11, 68-69].

Table 2.2. Hydrodynamic equations.

Author(s)	Equation
Wilke-Chang [9, 11, 61]	$D_{12,\mathrm{WC}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=7.4\times10^{-8}\dfrac{T\sqrt{\phi_1 M_1}}{\eta_1 V_{\mathrm{bp,2}}^{0.6}}$ (2.92) ϕ_1 is a dimensionless association factor of the solvent, η_1 is the solvent viscosity (cP), M_1 is the solvent molecular weight ($\mathrm{g\cdot mol^{-1}}$), $V_{\mathrm{bp,2}}$ is solute molar volume at its normal boiling point ($\mathrm{cm^3\cdot mol^{-1}}$).
Tyn-Calus [9, 62]	$D_{12,\mathrm{TC}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\left(\dfrac{V_{\mathrm{bp,2}}}{V_{\mathrm{bp,1}}^2}\right)^{1/6}\left(\dfrac{\mathbf{P_1}}{\mathbf{P_2}}\right)^{0.6}\dfrac{T}{\eta_1}$ (2.93) $\mathbf{P}_i$ identifies the parachor of component i, which is related with the liquid surface tension and may be estimated by additive group contributions. For most organic solvents, the following approximation is used in the calculation: $D_{12,\mathrm{TC}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\dfrac{V_{\mathrm{bp,1}}^{0.267}}{V_{\mathrm{bp,2}}^{0.433}}\dfrac{T}{\eta_1}$ (2.94) where $V_{\mathrm{bp,1}}$ is the solvent molar volume at its normal boiling point ($\mathrm{cm^3\cdot mol^{-1}}$).
Scheibel [11, 63]	$D_{12,\mathrm{Scheib}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\dfrac{8.2\times10^{-8}T}{\eta_1 V_{\mathrm{bp,2}}^{1/3}}\left[1+\left(\dfrac{3V_{\mathrm{bp,1}}}{V_{\mathrm{bp,2}}}\right)^{2/3}\right]$ (2.95)
Reddy-Doraiswamy [11, 64]	$D_{12,\mathrm{RD}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\beta\times\dfrac{T\sqrt{M_1}}{\eta_1\left(V_{\mathrm{bp,1}}\,V_{\mathrm{bp,2}}\right)^{1/3}}$ (2.96) $V_{\mathrm{bp,1}}/V_{\mathrm{bp,2}}\leq1.5\ \Rightarrow\ \beta=10\times10^{-8}$ $V_{\mathrm{bp,1}}/V_{\mathrm{bp,2}}\leq1.5\ \Rightarrow\ \beta=8.5\times10^{-8}$ (2.97)
Lusis-Ratcliff [11, 65]	$D_{12,\mathrm{LR}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\dfrac{8.52\times10^{-8}T}{\eta_1 V_{\mathrm{bp,1}}^{1/3}}\left[1.40\left(\dfrac{V_{\mathrm{bp,1}}}{V_{\mathrm{bp,2}}}\right)^{1/3}+\left(\dfrac{V_{\mathrm{bp,1}}}{V_{\mathrm{bp,2}}}\right)\right]$ (2.98)
Lai-Tan [66]	$D_{12,\mathrm{LT}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=2.50\times10^{-7}\dfrac{T\sqrt{M_1}}{\left(10\times\eta_1\right)^{0.688}V_{\mathrm{c,2}}^{1/3}}$ (2.99)

2.2.5.4. Empirical and semi-empirical equations

The models presented above require a set of data for each pair of molecules in the mixture, namely molecular weights, critical properties, LJ force constants, molar volumes at normal boiling point, density, viscosity, etc. Nonetheless, some of these inputs could not be available, for a particular system, being necessary their calculation from appropriate correlations available in literature. Furthermore, some of them are specific for a physical state, and only applicable to either non-polar (at most weakly polar) or polar systems.

As an alternative, simple empirical and semi-empirical expressions obtained by fitting experimental data can be used to interpolate non available diffusivities [8, 70]. In 1998, Suárez *et al*. [70], showed the most typical trends and dependencies that emerged from experimental diffusivities. Frequently, D_{12} is plotted as a function of pressure, temperature, solvent density, solvent viscosity, solute molecular weight, and solute molar volume at normal boiling point. Figures 2.8a to 2.8f illustrate some of these typical relationships found in dense fluids that will be described in the following.

The operating conditions frequently fixed are temperature and pressure, which influence directly solvent density and viscosity. From Figure 2.8a it is possible to observe that increasing pressure at fixed temperature decreases the diffusivity, being this effect more pronounced at higher temperatures. But at fixed pressure, an increment of temperature enhances de diffusion coefficient due to the increase of the kinetic energy of the system (see Figure 2.8b). Both tendencies were combined by Pizarro *et al*. [71] for systems in supercritical carbon dioxide, as shown in the following equation:

$$D_{12} = a_1 + \frac{a_2}{P} + a_3 T + a_4 \frac{T}{P} \tag{2.100}$$

where a_1, a_2, a_3, and a_4 are specific parameters of the system fitted to experimental data.

The influence of the solvent density and viscosity on D_{12} is represented in Figures 2.8c and 2.8d, respectively. By increasing solvent density and viscosity, the diffusion coefficient decreases due to the higher number of molecular collisions and the smaller mean free path [1, 10]. A set of empirical and semi-empirical relations of this type has been also reviewed by Medina [8], such as:

$$\frac{D_{12}}{T} = b_1 + b_2\, \rho_1 \tag{2.101}$$

$$\frac{D_{12}}{T} = c_1 + \frac{c_2}{\eta_1} \tag{2.102}$$

where b_1 and b_2, and c_1 and c_2 are adjustable parameters. Alternatively to the Eq. (2.102), Funazukuri *et al.* [72] proposed another expression valid for supercritical and liquid states, considering that for a specific solute its self-diffusion and binary coefficient are well represented by the same equation, *i.e.* the fitted parameters are only solute--dependent:

$$\frac{D_{12}}{T} = \alpha\, \eta_1^{\beta} \tag{2.103}$$

where α and β are constants fitted to the experimental data.

Figures 2.8e and 2.8f present a general plot of diffusion coefficients as a function of solute properties, such as molecular weight and molar volume at normal boiling point, respectively. In both representations is possible to observe that diffusivity decreases increasing both solute properties. This is in agreement with expectations, as solutes with larger sizes and masses tend to diffuse at a slower rate under comparable conditions. In the kinetic theory of gases [3, 10] a similar dependence on solute molecular weight is suggested, and in hydrodynamic equations the effect of the solute in the diffusion process is taken into account by solute molar volume at its normal boiling point [9].

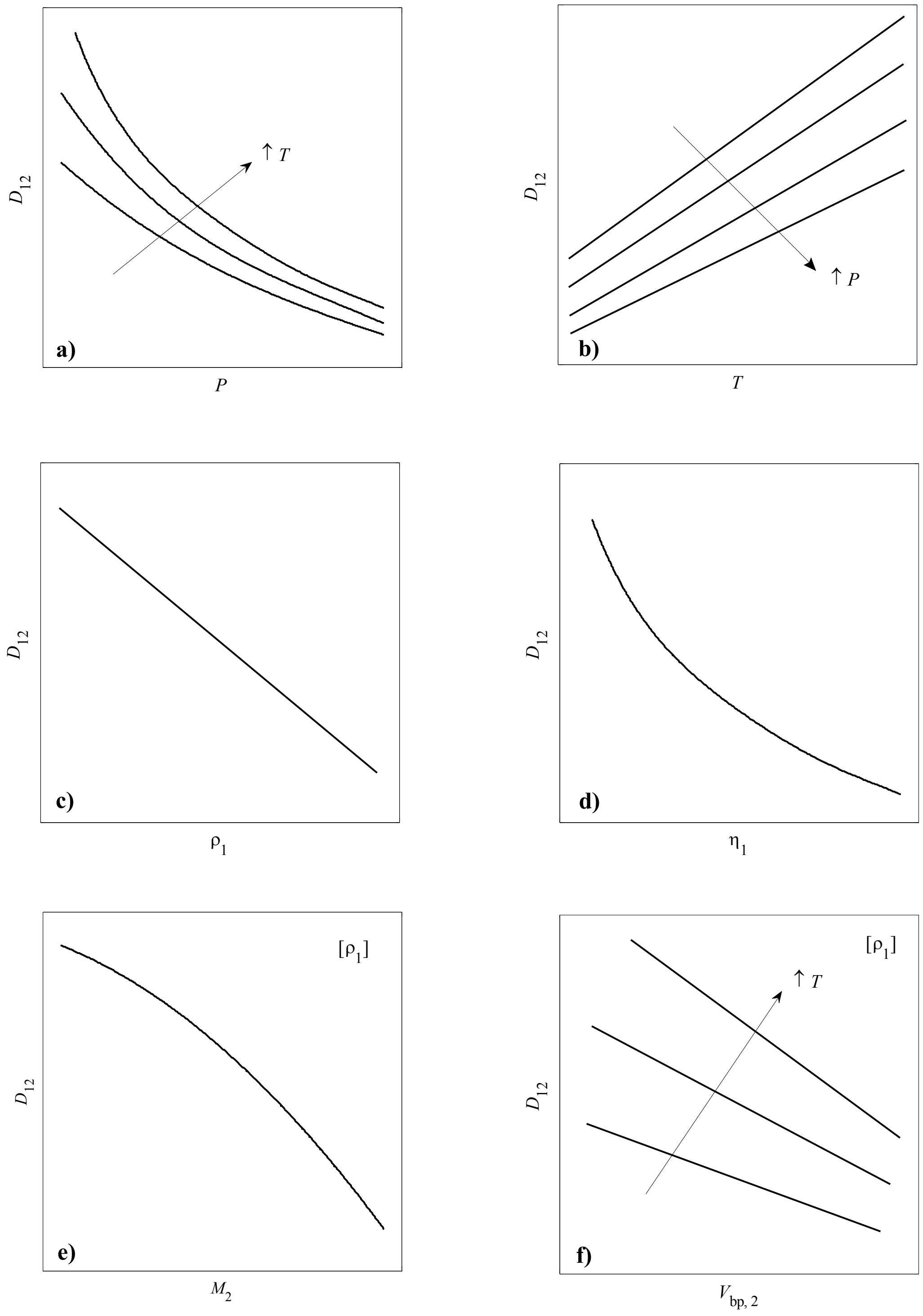

Figure 2.8. Typical behaviour of diffusion coefficients as a function of: a) pressure at different isotherms; b) temperature at different isobars; c) solvent density; d) solvent viscosity; e) solute molecular weight, at fixed density of the solvent; and f) solute molar volume at its normal boiling point, at fixed solvent density. Adapted from Suárez *et al.* [70].

Nomenclature

A	Parameter in Eq. (2.90)
A_{D}	Roughness factor
AARD	Average absolute relative deviation, $\mathrm{AARD} = \frac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left| \left(D_{12,\mathrm{Real}}^{\mathrm{calc}} - D_{12,\mathrm{Real}}^{\exp} \right) / D_{12,\mathrm{Real}}^{\exp} \right|_i$
B	Parameter in Eq. (2.87)
B'	Parameter in Eq. (2.90)
BAH	Ben-Amotz and Herschbach
b_i	Coefficients in Eq. (2.43)
BLSM	Boltzman-Liu-Silva-Macedo
D	Tracer diffusion coefficient
E_{a}	Activation energy
EHSD	Effective hard sphere diameter
F	Intermolecular force
F_{11}	Self-diffusion coefficient of HS fluid
F_{12}	Correction factor of HS system
$g(\sigma)$	Radial distribution function at contact
H_i	Functions in Eq. (2.43)
HS	Hard sphere
k_{B}	Boltzmann constant
k_{12}	Binary interaction parameter
LJ	Lennard-Jones
m	Mass of a molecule
M	Molecular weight
MD	Molecular Dynamics
MS	Maxwell-Stefan
NDP	Number of data points
NS	Number of systems
N_{a}	Avogadro constant
P	Pressure

$\mathbf{P}$	Parachor
r	Radial coordinate
$\mathfrak{R}_g$	Universal gas constant
RLJ	Repulsive Lennard-Jones
SS	Soft sphere
ST	Stockmayer
SW	Square well
T	Temperature
TLSM	Tracer Liu-Silva-Macedo
V	Molar volume
V_D	Parameter in Eq. (2.87)
V_i	Intrinsic molar volume
V_f	Molar free volume
WCA	Week-Chandler-Andersen

Greek letters

α and β	Parameters in Eq. (2.103)
α_{LJ}	Parameter in Eq. (2.63) and (2.64)
γ and γ_B	Parameters in Eq. (2.27)
ε/k_B	Lennard-Jones energy parameter
ζ	Friction coefficient
η	Viscosity
θ_a , θ_b	Angles of inclination of the dipoles axes
λ	Thermal conductivity
μ	Dipole moment
ρ	Number density, N_a/V
σ	Molecular diameter
φ_1	HS packing fraction of solvent
ϕ	Intermolecular potential
ψ	Azimuthal angle between angles θ_a and θ_b
ω	Acentric factor

Subscripts

bp	Boiling point
BAH	Ben-Amotz and Herschbach
c	Critical property
d	Refers to diameter correlation in TLSM model
Dym	Dymond's model
eff	Effective hard sphere diameter (EHSD)
E	Enskog
en	Refers to energy correlation in TLSM model
HS	Hard sphere fluid
LJ	Lennard-Jones fluid
r	Reduced property
R	Repulsive contribution
Real	Real system
S	Soft attractive contribution
SS	Soft sphere fluid
ST	Stockmayer fluid
SW	Square-well fluid
TLSM	Tracer Liu-Silva-Macedo model
TRL	Tracer Liu and Ruckenstein model
WCA	Week-Chandler-Andersen fluid
Zhu	Zhu *et al*. model
1, 11	Solvent
2	Solute
12	Binary property

Superscripts

0	Ideal gas
*	Reduced quantity

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3. Database and Properties

In this work the largest database of binary diffusion coefficients at infinite dilution in liquid, gas and supercritical solvents published up till now has been compiled with the purpose to validate the new models developed (see Chapter 4). It comprehends 622 binary systems containing 9407 data points where polar/non-polar, symmetrical/asymmetrical, small/large, and light/heavy molecules are included without exception. In Table 3.1 detailed information about database is given: systems studied, ranges of reduced temperature, pressure and solvent density (reduction performed with the critical constants), number of data points (NDP), and data sources. As much as possible, all data published were selected, but graphical information was rejected. Table 3.2 contains the name, molecular formula, CAS number, molecular weight, critical constants (T_c, P_c and V_c), and molar volume at normal boiling point (V_{bp}) for all molecules involved in calculations (358 totally). The involved data sources are also identified.

The solvent densities and viscosities reported together with the diffusivity data were always used. In contrast, when those properties were omitted they were taken from NIST [1] and DIPPR [2] databases or calculated by appropriate correlations: Yaws [3], Cibulka and Ziková [4], Cibulka *et al.* [5-6], Cibulka and Takagi [7], and Hankinson--Brobst-Thomson [8-10]. In the case of carbon dioxide the density and viscosity were estimated by the equations of Pitzer and Schreiber [11] and Altunin and Sakhabetdinov [12], respectively; for water they were calculated by IAPWS-IF97 [13]. The critical constants were taken from Reid *et al.* [10] Yaws [3, 14], Liu and Ruckenstein [15], DIPPR [2] and Korea Thermophysical Properties Data Bank (KDB) [16] databases, but they are unavailable they were estimated by Joback [10, 17-18], Ambrose [10, 19-20], Klincewicz [10, 21], Somayajulu [22], Wen-Qiang [23], Constantinou-Gani [24] methods. For ionic liquids, the critical constants were taken from Valderrama and Rojas [25]. The molar volumes at their normal boiling point were estimated by Tyn-Calus equation [10, 26].

Table 3.1. Database of binary diffusion coefficients at infinite dilution of solutes (2) in solvents (1): experimental ranges of reduced temperature, pressure and density, number of data points (NDP) and data sources.

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
acetone	benzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	6	[27]
acetone	biphenyl	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	6	[27]
acetone	chlorobenzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	6	[27]
acetone	ethylbenzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	6	[27]
acetone	naphthalene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	5	[27]
acetone	*n*-propylbenzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	5	[27]
acetone	toluene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	5	[27]
acetone	1,2,4-trichlorobenzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	6	[27]
acetone	1,3,5-trimethylbenzene	0.5278 – 0.6459	0.0213	2.69724 – 2.94928	5	[27]
acetone	water	0.5868 – 0.6458	0.0213	2.69746 – 2.82699	4	[28]
acetonitrile	carbon disulphide	0.5467 – 0.5467	0.0207 – 63.3954	3.27232 – 3.85671	5	[29]
acetonitrile	methanol	0.5192 – 0.5742	0.0207 – 46.5010	3.20335 – 3.71189	20	[29]
acetonitrile	[Bmim][bti][a]	0.5188 – 0.6104	0.0207	3.11034 – 3.34117	5	[30]
acetonitrile	[Emim][bti][b]	0.5188 – 0.6104	0.0207	3.11034 – 3.34117	5	[30]
acetonitrile	[Hmim][bti][c]	0.5188 – 0.6104	0.0207	3.11034 – 3.34117	5	[30]
acetonitrile	[Omim][bti][d]	0.5188 – 0.6104	0.0207	3.11034 – 3.34117	5	[30]
acetylene	helium	0.9080 – 1.2970	0.0170	0.00340 – 0.00490	7	[31]
argon	*i*-butane	2.0350 – 4.4640	0.0210	0.00140 – 0.00300	8	[32]
argon	*n*-butane	2.0320 – 4.4640	0.0210	0.00140 – 0.00300	8	[32]
argon	ethane	2.0350 – 4.4640	0.0210	0.00140 – 0.00300	9	[32]
argon	helium	0.7820 – 3.3030	0.0210	0.00180 – 0.00770	49	[33-37]
argon	hydrogen	0.7820 – 1.9630	0.0210	0.00310 – 0.00770	5	[35]
argon	krypton	1.3260 – 2.6530	0.0210	0.00230 – 0.00460	11	[38]
argon	methane	2.0430 – 4.4640	0.0210	0.00140 – 0.00300	9	[32]
argon	neon	0.7820 – 9.0410	0.0210	0.00070 – 0.00770	25	[35-36, 39]
argon	propane	2.0270 – 4.5030	0.0210	0.00130 – 0.00300	9	[32]
1,3-butadiene	helium	0.6590 – 0.9410	0.0240	0.00670 – 0.00960	7	[31]
n-butane	helium	0.6590 – 0.9410	0.0270	0.00790 – 0.01170	7	[31]
1-butanol	ammonia	0.5295 – 0.6183	0.0385 – 3.5090	2.84412 – 3.01516	64	[40]
1-butanol	carbon dioxide	0.5295 – 0.6183	0.0588 – 3.4548	2.81593 – 3.01516	66	[40]
1-butanol	propane	0.5295 – 0.6183	0.0611 – 3.7511	2.82594 – 3.02109	98	[40]
1-butanol	propene	0.5295 – 0.6184	0.0226 – 3.9389	2.81964 – 3.03111	135	[40]
carbon dioxide	acetone	0.9969 – 1.0955	1.0759 – 5.4350	0.77207 – 2.07624	214	[41-45]
carbon dioxide	acridine	1.0133 – 1.0791	2.3374 – 3.7344	1.51487 – 1.95636	6	[46]
carbon dioxide	adamantanone	1.0307	1.3550 – 2.0325	1.33044 – 1.66214	8	[47]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
carbon dioxide	allylbenzene	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[48]
carbon dioxide	aniline	1.0298 – 1.0956	2.0325 – 4.7425	1.29589 – 1.91043	15	[49]
carbon dioxide	anisole	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[50]
carbon dioxide	anthracene	1.0293 – 1.0950	14.4986 – 47.4255	0.76810 – 1.99492	22	[51]
carbon dioxide	arachidonic acid (AA)	1.0133 – 1.1284	1.2873 – 4.1314	1.18797 – 1.98904	75	[52]
carbon dioxide	AA ethyl ester	1.0133 – 1.1120	1.1409 – 4.0583	1.06846 – 1.81567	48	[53]
carbon dioxide	behenic acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	17	[54]
carbon dioxide	benzene	0.9969 – 1.0955	1.0840 – 4.7425	0.59522 – 1.99602	249	[41, 55-62]
carbon dioxide	benzoic acid	0.9640 – 1.0791	0.9621 – 4.0650	1.14645 – 1.95636	35	[46, 63-65]
carbon dioxide	benzyl acetate	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[66]
carbon dioxide	benzylacetone	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[67]
carbon dioxide	biphenyl	0.9640 – 1.0626	0.9623 – 2.3169	1.14788 – 1.94585	24	[65]
carbon dioxide	2-bromoanisole	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[48]
carbon dioxide	bromobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	21	[68-69]
carbon dioxide	2-butanone	1.0133 – 1.0791	1.1287 – 4.6789	1.24269 – 2.02871	40	[42, 69-70]
carbon dioxide	*N*-(4-methoxybenzylidene)- -4-*n*-butylaniline	1.0307	1.6260 – 2.1680	1.52714 – 1.69369	5	[47]
carbon dioxide	*n*-butylbenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29531 – 1.99727	15	[71]
carbon dioxide	*tert*-butylbenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[72]
carbon dioxide	butyric acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	16	[73-74]
carbon dioxide	caffeine	1.0128 – 1.0955	1.0881 – 2.2846	0.91997 – 1.72280	25	[75-77]
carbon dioxide	capric acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	16	[73-74]
carbon dioxide	caprylic acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	16	[73-74]
carbon dioxide	β-carotene	1.0133 – 1.0955	1.2358 – 4.1111	1.33461 – 1.98745	90	[78-80]
carbon dioxide	L-carvone	1.0133 – 1.1120	2.0325 – 4.0650	1.38940 – 1.98382	27	[81-82]
carbon dioxide	chlorobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	21	[68-69]
carbon dioxide	chrysene	0.9969 – 1.0955	2.1680 – 3.5908	1.70688 – 1.87757	4	[41]
carbon dioxide	citral	1.0298 – 1.0955	1.6260 – 2.7100	0.95300 – 1.79863	15	[83]
carbon dioxide	cobalt(III) acetylacetonate	1.0298 – 1.0955	1.3144 – 5.4201	1.28832 – 2.04129	38	[84]
carbon dioxide	copper(II) trifluoroacetylacetonate	1.0133 – 1.0462	1.4661 – 2.2425	1.28443 – 1.75894	12	[85]
carbon dioxide	15-crown-5	1.0134 – 1.0299	1.1883 – 4.0705	0.89973 – 1.94298	29	[86]
carbon dioxide	dibenzo-24-crown-8	1.0134 – 1.0299	2.0339 – 4.7425	1.66636 – 2.02373	28	[86]
carbon dioxide	cycloheptanone	1.0330	1.3550 – 2.4390	1.29705 – 1.73773	8	[87]
carbon dioxide	cyclononanone	1.0330	1.3550 – 2.4390	1.29705 – 1.73773	8	[87]
carbon dioxide	cyclopentanone	1.0330	1.3550 – 2.4390	1.29705 – 1.73773	8	[87]
carbon dioxide	*n*-decane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	dibenzyl ether	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[66]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
carbon dioxide	1,2-dichlorobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[72]
carbon dioxide	1,3-dichlorobenzene	1.0298	2.0325 – 3.2520	1.66680 – 1.86317	4	[82]
carbon dioxide	*p*-dichlorobenzene	0.9804 – 1.0462	1.2519 – 2.3169	1.14788 – 1.86691	13	[65]
carbon dioxide	diethyl ether	1.0298 – 1.0955	1.0984 – 2.1967	0.41819 – 1.70411	17	[69-70, 89]
carbon dioxide	1,2-diethylbenzene	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[90]
carbon dioxide	1,4-diethylbenzene	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[90]
carbon dioxide	diisopropyl ether	1.0298 – 1.0955	1.0984 – 2.1967	0.41819 – 1.70411	15	[89]
carbon dioxide	2,3-dimethylaniline	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[91]
carbon dioxide	2,6-dimethylaniline	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[91]
carbon dioxide	1,1'-dimethylferrocene	1.0133 – 1.0626	1.1138 – 5.4363	0.82775 – 2.07666	68	[92]
carbon dioxide	2,6-dimethylnaphthalene	1.0135	1.2331 – 2.6423	1.42716 – 1.83924	6	[93-94]
carbon dioxide	2,7-dimethylnaphthalene	1.0135	1.4499 – 2.7100	1.57070 – 1.84816	6	[93-94]
carbon dioxide	2,4-dimethylphenol	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[50]
carbon dioxide	diolein	1.0300	1.3550 – 3.3889	1.34136 – 1.87770	9	[95]
carbon dioxide	1,3-divinylbenzene	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[48]
carbon dioxide	docosahexaenoic acid (DHA)	1.0133 – 1.1284	1.2561 – 4.0827	1.21898 – 1.98489	63	[96]
carbon dioxide	DHA ethyl ester	1.0128 – 1.1120	1.1409 – 4.0583	1.06851 – 1.81570	65	[53-54]
carbon dioxide	DHA methyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	17	[54]
carbon dioxide	*n*-dodecane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	eicosapentaenoic acid (EPA)	1.0133 – 1.1284	1.1762 – 4.0854	1.15708 – 1.95136	55	[96]
carbon dioxide	EPA ethyl ester	1.0133 – 1.1120	1.1409 – 4.0583	1.06846 – 1.81567	48	[53]
carbon dioxide	EPA methyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	17	[54]
carbon dioxide	ethanol	1.0300	1.2873 – 3.3875	1.23600 – 1.87755	24	[63]
carbon dioxide	ethyl acetate	1.0128 – 1.0786	1.0244 – 2.1680	0.45553 – 1.72309	16	[70, 75]
carbon dioxide	ethylbenzene	1.0298 – 1.0955	2.0325 – 4.7425	1.29531 – 1.99727	15	[57]
carbon dioxide	ethyl benzoate	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[67]
carbon dioxide	2-ethyltoluene	1.0293 – 1.0950	2.0325 – 4.7425	1.29589 – 1.91043	15	[97]
carbon dioxide	ethylene	0.9810 – 1.1450	0.1460 – 2.7520	0.03650 – 1.68550	48	[98]
carbon dioxide	3-ethyltoluene	1.0293 – 1.0950	2.0325 – 4.7425	1.29589 – 1.91043	15	[97]
carbon dioxide	4-ethyltoluene	1.0293 – 1.0950	2.0325 – 4.7425	1.29589 – 1.91043	15	[97]
carbon dioxide	eugenol	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[67]
carbon dioxide	ferrocene	1.0133 – 1.0955	1.0867 – 5.4661	0.60020 – 2.07714	107	[92, 99]
carbon dioxide	2-fluoroanisole	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[48]
carbon dioxide	fluorobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29589 – 1.91043	15	[68]
carbon dioxide	3-fluorophenol	1.0298	2.0325 – 3.2520	1.66680 – 1.86317	4	[82]
carbon dioxide	geraniol	1.0298	2.0325 – 3.2520	1.66680 – 1.86317	4	[82]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
carbon dioxide	helium	0.6420 – 1.6380	0.0140	0.00230 – 0.00570	56	[33-34, 37, 100-103]
carbon dioxide	*n*-heptane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	2-heptanone	1.0340	1.4228 – 2.4390	1.36368 – 1.73393	11	[47]
carbon dioxide	4-heptanone	1.0307	1.3550 – 2.1680	1.33044 – 1.69369	9	[47]
carbon dioxide	hexachlorobenzene	1.0128 – 1.0786	1.3103 – 3.3523	0.86978 – 1.92233	14	[104]
carbon dioxide	1-hexadecene	1.0298 – 1.2271	1.3550 – 4.0650	0.91313 – 1.94292	11	[105]
carbon dioxide	1,1,1,5,5,5- -hexafluoroacetylacetone	1.0133 – 1.0462	1.4106 – 3.0081	1.21018 – 1.86989	15	[85]
carbon dioxide	*n*-hexane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	hydrogen	1.0370 – 1.1310	0.0140	0.00330 – 0.00360	7	[100]
carbon dioxide	iodobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	20	[68-69]
carbon dioxide	D-limonene	1.0298 – 1.0955	1.6260 – 2.7100	0.95300 – 1.79863	15	[83]
carbon dioxide	linalool	1.0298 – 1.0955	1.6260 – 2.7100	0.95300 – 1.79863	15	[56]
carbon dioxide	linoleic acid	1.0133 – 1.1284	1.1518 – 4.1057	1.18797 – 1.98703	71	[52]
carbon dioxide	*α*-linolenic acid	1.0133 – 1.1284	1.1518 – 4.0840	1.16293 – 1.98446	56	[96]
carbon dioxide	*γ*-linolenic acid	1.0133 – 1.1284	1.1762 – 4.1328	0.97583 – 1.94819	142	[106]
carbon dioxide	*γ*-linolenic acid ethyl ester	1.0300 – 1.1284	1.1382 – 2.1694	0.71647 – 1.69741	41	[106]
carbon dioxide	linoleic acid methyl ester	1.0135 – 1.0793	1.8970 – 4.5528	1.57673 – 1.98212	21	[107-108]
carbon dioxide	*γ*-linolenic acid methyl ester	1.0298 – 1.1284	1.0989 – 4.5528	0.62225 – 1.98207	52	[106-107]
carbon dioxide	L-menthone	1.0133 – 1.1120	2.0325 – 4.0650	1.38940 – 1.98382	23	[81]
carbon dioxide	methanol	1.0300	1.2873 – 2.8455	1.23600 – 1.81208	10	[63]
carbon dioxide	2-methylanisole	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[91]
carbon dioxide	4-methylanisole	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[91]
carbon dioxide	1-methylnaphthalene	1.0298 – 1.2271	1.3550 – 4.0650	0.91313 – 1.94292	11	[105]
carbon dioxide	methyl orange	0.9640 – 1.0298	1.1924 – 3.0759	1.28832 – 2.03170	60	[109]
carbon dioxide	monoolein	1.0300	1.3564 – 3.3875	1.34299 – 1.87755	11	[95]
carbon dioxide	myristic acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	16	[73-74]
carbon dioxide	myristoleic acid	1.0300 – 1.1284	1.2466 – 4.0650	0.97697 – 1.87755	42	[110]
carbon dioxide	myristoleic acid methyl ester	1.0298 – 1.1284	1.0840 – 3.3875	0.48065 – 1.87812	81	[110-111]
carbon dioxide	naphthalene	0.9479 – 1.0955	0.9106 – 13.5501	0.46956 – 2.37385	114	[41, 77, 93, 99, 112]
carbon dioxide	1-naphthol	1.0128 – 1.0457	1.4363 – 2.1951	1.13081 – 1.74529	11	[51]
carbon dioxide	2-naphthol	1.0128 – 1.0786	1.3415 – 2.0596	0.70196 – 1.71755	16	[51]
carbon dioxide	2-nitroanisole	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[72]
carbon dioxide	nitrobenzene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	23	[50, 69]
carbon dioxide	3-nitrotoluene	1.0293 – 1.0950	2.0325 – 4.7425	1.29553 – 1.99715	15	[91]
carbon dioxide	*n*-nonane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	2-nonanone	1.0340	1.3550 – 2.0325	1.28201 – 1.64641	10	[47]

Table 3.1 (*Continued*)

System		$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
Solvent (1)	Solute (2)					
carbon dioxide	5-nonanone	1.0340	1.3550 – 2.4390	1.28201 – 1.73393	12	[47]
carbon dioxide	*n*-octane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	oleic acid	1.0300	1.2818 – 4.0786	1.22463 – 1.94359	19	[95]
carbon dioxide	oleic acid ethyl ester	1.0300	1.1653 – 1.4905	0.80523 – 1.45943	5	[95]
carbon dioxide	oleic acid methyl ester	1.0293 – 1.0300	1.0840 – 2.1680	0.59385 – 1.70011	21	[95, 107, 113]
carbon dioxide	palladium(II) acetylacetonate	1.0133 – 1.1284	1.1518 – 5.4201	1.20158 – 2.07571	125	[84]
carbon dioxide	palmitic acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	17	[114]
carbon dioxide	*n*-pentane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	2-pentanone	1.0133 – 1.0342	1.2033 – 3.9634	1.18413 – 1.93408	23	[42]
carbon dioxide	3-pentanone	1.0133 – 1.0791	1.1721 – 4.6843	1.26087 – 2.02871	46	[42, 87]
carbon dioxide	2,4-dimethyl-3-pentanone	1.0330	1.3550 – 2.4390	1.29705 – 1.73773	8	[47]
carbon dioxide	2,2,4,4-tetramethyl-3--pentanone	1.0307	1.3550 – 2.1680	1.33044 – 1.69369	9	[47]
carbon dioxide	*n*-pentylbenzene	1.0128 – 1.3088	2.0325 – 4.7425	1.29553 – 2.03431	31	[71]
carbon dioxide	phenanthrene	0.9969 – 1.0955	1.3076 – 3.7344	1.08209 – 1.95636	25	[41, 46, 104]
carbon dioxide	phenol	1.0128 – 1.0791	1.0894 – 4.1030	0.75743 – 1.98681	109	[44, 63, 75, 79-80]
carbon dioxide	phenylacetic acid	1.0133 – 1.0462	1.3103 – 2.8523	1.28016 – 1.81357	16	[115]
carbon dioxide	phenylacetylene	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[90]
carbon dioxide	phenylbutazone	1.0133 – 1.1284	1.1518 – 5.4201	0.95063 – 2.07442	78	[116]
carbon dioxide	1-phenyldodecane	1.0293 – 1.0950	2.0325 – 4.7425	1.29531 – 1.99727	15	[71]
carbon dioxide	1-phenylethanol	1.0298 – 1.0956	2.0325 – 4.7425	1.29553 – 1.99787	15	[117]
carbon dioxide	2-phenylethanol	1.0298 – 1.0956	2.0325 – 4.7425	1.29553 – 1.99787	15	[117]
carbon dioxide	2-phenylethyl acetate	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[66]
carbon dioxide	1-phenylhexane	1.0293 – 1.0950	2.0325 – 4.7425	1.29531 – 1.99727	15	[71]
carbon dioxide	phenylmethanol	1.0298 – 1.0956	2.0325 – 4.7425	1.29553 – 1.99787	15	[117]
carbon dioxide	1-phenyloctane	1.0293 – 1.0950	2.0325 – 4.7425	1.29531 – 1.99727	15	[71]
carbon dioxide	3-phenylpropyl acetate	1.0298 – 1.0956	2.0325 – 4.7425	1.29531 – 1.99727	15	[66]
carbon dioxide	α-pinene	1.0298 – 1.0955	1.6260 – 2.7100	0.95300 – 1.79863	15	[118]
carbon dioxide	β-pinene	1.0298 – 1.0955	1.6260 – 2.7100	0.95300 – 1.79863	15	[118]
carbon dioxide	2-phenyl-1-propanol	1.0298 – 1.0956	2.0325 – 4.7425	1.29553 – 1.99787	15	[117]
carbon dioxide	3-phenyl-1-propanol	1.0298 – 1.0956	2.0325 – 4.7425	1.29553 – 1.99787	15	[117]
carbon dioxide	1-propanol	1.0300	1.2873 – 2.1680	1.23600 – 1.69712	17	[63]
carbon dioxide	2-propanol	1.0300	1.2873 – 2.3035	1.23600 – 1.72474	18	[63]
carbon dioxide	*i*-propylbenzene	1.0298 – 1.0955	1.7615 – 4.7425	1.08209 – 1.99602	36	[41, 57, 70, 119]
carbon dioxide	*n*-propylbenzene	1.0133 – 1.0955	1.1518 – 4.7425	0.76383 – 1.99727	60	[55, 57, 70, 119]
carbon dioxide	pyrene	0.9969 – 1.0955	1.5583 – 47.4255	0.83211 – 1.98852	21	[41, 51]
carbon dioxide	squalene	1.0340	1.7615 – 2.4390	1.56207 – 1.73393	5	[47]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
carbon dioxide	stearic acid	1.0309 – 1.0309	1.7615 – 2.1680	1.58097 – 1.69297	4	[47]
carbon dioxide	stearic acid ethyl ester	1.0128 – 1.0457	1.3103 – 2.8523	1.28016 – 1.81357	17	[54]
carbon dioxide	styrene	1.0298 – 1.0956	2.0325 – 4.7425	1.29589 – 1.91043	15	[49]
carbon dioxide	*n*-tetradecane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	tetrahydrofuran	1.0298 – 1.0955	1.0984 – 2.1967	0.41819 – 1.70411	15	[89]
carbon dioxide	thenoyltrifluoroacetone	1.0133 – 1.0462	1.4295 – 3.0366	1.21018 – 1.88696	15	[85]
carbon dioxide	α-tocopherol	1.0133 – 1.0955	1.1531 – 4.1070	1.31130 – 1.98713	82	[78-80]
carbon dioxide	toluene	1.0066 – 1.0955	1.0894 – 4.7425	0.96866 – 1.99727	35	[57, 61, 75]
carbon dioxide	triarachidonin	1.0300	1.3482 – 4.0976	1.33304 – 1.94521	27	[120]
carbon dioxide	trierucin	1.0133 – 1.0626	1.1192 – 4.0732	1.20406 – 1.98404	101	[120]
carbon dioxide	trifluoroacetylacetone	1.0133 – 1.0462	1.4485 – 2.9241	1.23749 – 1.87309	15	[85]
carbon dioxide	1,3,5-trimethylbenzene	0.9969 – 1.0956	1.2873 – 4.7425	1.23991 – 1.99595	34	[41, 49, 55, 69]
carbon dioxide	trinervonin	1.0133 – 1.0626	1.2195 – 4.0718	1.26796 – 1.98414	38	[120]
carbon dioxide	triolein	0.9803 – 1.0300	1.2371 – 3.4011	1.10114 – 2.01472	14	[64, 120]
carbon dioxide	ubiquinone CoQ10	1.0133 – 1.0955	1.1531 – 4.0949	1.31130 – 1.98436	80	[80, 121]
carbon dioxide	*n*-undecane	0.9837 – 1.0133	1.2195 – 1.4228	1.55921 – 1.74504	5	[88]
carbon dioxide	6-undecanone	1.0340	1.3550 – 2.4390	1.28201 – 1.73393	13	[47]
carbon dioxide	vanillin	1.0133 – 1.0462	1.3957 – 2.8523	1.28016 – 1.81357	15	[115]
carbon dioxide	vitamin K_1	1.0299	1.3550 – 4.0650	1.34181 – 1.94251	17	[86, 111]
carbon dioxide	vitamin K_3	1.0298	1.2141 – 4.0678	1.01768 – 1.94316	22	[80, 108, 111]
carbon dioxide	water	0.9311 – 1.0133	1.7886 – 4.0379	1.69468 – 2.17594	24	[122]
carbon dioxide	*m*-xylene	1.0298 – 1.2271	1.3550 – 4.0650	0.40289 – 1.94292	12	[105]
carbon dioxide	5-*tert*-butyl-*m*-xylene	1.0134 – 1.3093	2.0325 – 4.7425	1.29210 – 2.03313	31	[90]
carbon dioxide	*p*-xylene	1.0298 – 1.0626	2.0325 – 3.3875	1.49577 – 1.87812	7	[69-70]
carbon monoxide	helium	2.3720 – 2.5880	0.0290	0.00330 – 0.00360	7	[100]
carbon monoxide	hydrogen	2.3720 – 2.5880	0.0290	0.00330 – 0.00360	7	[100]
chlorobenzene	propene	0.4715 – 0.5506	0.0259 – 1.3874	2.86304 – 3.02640	32	[123-124]
chlorotrifluoromethane	acetone	1.0369	1.1499 – 2.0930	0.67588 – 1.64161	10	[125]
chlorotrifluoromethane	1,3-dibromobenzene	1.0535	1.2222 – 2.8191	0.67715 – 1.71929	12	[125]
chlorotrifluoromethane	*p*-xylene	1.0535	1.2222 – 2.8191	0.67715 – 1.71929	8	[125]
cyclohexane	acetone	0.5478 – 0.6020	3.9312 – 3.9312	2.76666 – 2.86181	4	[126]
cyclohexane	argon	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	benzene	0.5388 – 0.9453	3.9312; sat.p[e]	1.75661 – 2.86181	12	[126, 128]
cyclohexane	carbon tetrachloride	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	1,1'-dimethylferrocene	0.5658 – 0.5838	0.0467 – 4.6732	2.78010 – 2.84147	5	[129]
cyclohexane	ethane	0.5068 – 0.6562	–	2.59466 – 2.90573	5	[130]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
cyclohexane	ethylene	0.5068 – 0.6562	–	2.59466 – 2.90573	5	[130]
cyclohexane	ethylferrocene	0.5658 – 0.5838	0.0418 – 4.6732	2.78002 – 2.84147	6	[129]
cyclohexane	ferrocene	0.5658 – 0.5838	0.0467 – 4.6732	2.78010 – 2.84147	5	[129]
cyclohexane	krypton	0.5659 – 0.7513	–	2.38606 – 2.78130	6	[127]
cyclohexane	methane	0.5659 – 0.7513	–	2.38606 – 2.78130	6	[127]
cyclohexane	naphthalene	0.5388 – 0.9453	3.9312; sat.p^{e}	1.75661 – 2.86181	12	[126, 128]
cyclohexane	phenanthrene	0.5388 – 0.9453	sat.p^{e}	1.75661 – 2.83254	8	[128]
cyclohexane	tetrabutyltin	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	tetraethyltin	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	tetramethyltin	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	tetrapropyltin	0.5387 – 0.7513	–	2.38606 – 2.83254	6	[127]
cyclohexane	toluene	0.5388 – 0.9453	3.9312; sat.p^{e}	1.75661 – 2.86181	12	[126, 128]
cyclohexane	1,3,5-trimethylbenzene	0.5388 – 0.9453	3.9312; sat.p^{e}	1.75661 – 2.86181	12	[126, 131]
cyclohexane	xenon	0.5387 – 0.7513	–	2.38606 – 2.83254	7	[127]
cyclohexane	*m*-xylene	0.5478 – 0.6020	3.9312	2.76666 – 2.86181	4	[126]
cyclohexane	*p*-xylene	0.5388 – 0.9453	sat.p^{e}	1.75661 – 2.83254	8	[128]
n-decane	argon	0.4828 – 0.7018	–	2.60778 – 3.08318	3	[132]
n-decane	carbon tetrachloride	0.4828 – 0.6048	–	2.8298 – 3.08318	3	[132]
n-decane	12-crown-4	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	15-crown-5	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	18-crown-6	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	dicyclohexano-18-crown-6	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	dicyclohexano-24-crown-8	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	krypton	0.4820 – 0.7010	–	2.60770 – 3.08310	3	[132]
n-decane	methane	0.4820 – 0.7010	–	2.60770 – 3.08310	3	[132]
n-decane	tetrabutyltin	0.4824 – 0.7010	0.0478	2.61426 – 3.07946	4	[132]
n-decane	tetraethyltin	0.482 – 0.701	–	2.6077 – 3.0831	3	[132]
n-decane	tetramethyltin	0.4824 – 0.7010	0.0478	2.61426 – 3.07946	4	[132]
n-decane	tetrapropyltin	0.4824 – 0.7010	0.0478	2.61426 – 3.07946	4	[132]
n-decane	*s*-trioxane	0.4828 – 0.6042	0.0478	2.82853 – 3.07882	4	[133]
n-decane	xenon	0.4584 – 0.7010	0.0478	2.61426 – 3.12838	8	[132, 134]
deuterium	hydrogen	2.9950 – 7.6820	0.0610	0.00250 – 0.00640	5	[35]
deuterium oxide	oxygen	0.4300 – 0.5742	0.0046	2.91053 – 3.10444	18	[135]
2,3-dimethylbutane	benzene	1.0464 – 1.0964	1.7099 – 5.0799	1.43200 – 1.90832	11	[136]
2,3-dimethylbutane	naphthalene	1.0464 – 1.0964	1.7099 – 5.0799	1.43200 – 1.90832	9	[136]
2,3-dimethylbutane	phenanthrene	1.0464 – 1.0964	1.7099 – 5.0799	1.43200 – 1.90832	11	[136]

Table 3.1 (*Continued*)

System		$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
Solvent (1)	Solute (2)					
2,3-dimethylbutane	toluene	1.0464 – 1.0964	2.0051 – 5.0799	1.43200 – 1.90832	10	[136]
n-dodecane	acetone	0.4607 – 0.5214	8.7912	3.04032 – 3.15283	5	[126]
n-dodecane	benzene	0.4607 – 0.5062	8.7912	3.06824 – 3.15283	4	[126]
n-dodecane	carbon dioxide	0.4621 – 0.8617	0.7654 – 1.8978	2.16487 – 3.10700	9	[137]
n-dodecane	carbon monoxide	0.4621 – 0.8617	0.7654 – 1.8978	2.16487 – 3.10700	9	[137]
n-dodecane	*n*-decane	0.4619 – 0.8599	0.7760 – 0.7960	2.18956 – 3.10666	5	[138]
n-dodecane	*n*-hexadecane	0.4619 – 0.8599	0.7760 – 0.7960	2.18956 – 3.10666	5	[138]
n-dodecane	hydrogen	0.4621 – 0.8617	0.7654 – 1.8978	2.16487 – 3.10700	9	[137]
n-dodecane	linoleic acid methyl ester	0.4607 – 0.5062	8.7912	3.06824 – 3.15283	4	[126]
n-dodecane	naphthalene	0.4607 – 0.5214	8.7912	3.04032 – 3.15283	5	[126]
n-dodecane	*n*-octane	0.4619 – 0.8599	0.7760 – 1.8900	2.18956 – 3.10666	9	[138]
n-dodecane	*n*-tetradecane	0.4619 – 0.8599	0.7760 – 0.7960	2.18956 – 3.10666	5	[138]
n-dodecane	toluene	0.4608 – 0.5062	8.7912	3.06824 – 3.15283	4	[126]
n-dodecane	1,3,5-trimethylbenzene	0.4607 – 0.5062	8.7912	3.06824 – 3.15283	4	[126]
n-dodecane	vitamin K_3	0.4607 – 0.5062	8.7912	3.06815 – 3.15187	4	[126]
n-dodecane	*m*-xylene	0.4607 – 0.5062	8.7912	3.06824 – 3.15283	4	[126]
n-eicosane	carbon dioxide	0.4879 – 0.6955	1.2257	2.64528 – 3.10644	5	[139]
n-eicosane	carbon monoxide	0.4879 – 0.6955	1.2257	2.64528 – 3.10644	5	[139]
n-eicosane	*n*-dodecane	0.4889 – 0.6956	1.2257	2.64486 – 3.10644	5	[139]
n-eicosane	*n*-hexadecane	0.4889 – 0.6956	1.2257	2.64486 – 3.10644	5	[139]
n-eicosane	hydrogen	0.4879 – 0.6955	1.2257	2.64528 – 3.10644	5	[139]
n-eicosane	*n*-octane	0.4889 – 0.6956	1.2257	2.64486 – 3.10644	5	[139]
ethane	helium	0.9170 – 1.3100	0.0210	0.00460 – 0.00660	7	[31]
ethane	nitrogen	1.0220 – 2.1980	0.0210	0.00270 – 0.00580	14	[100, 140]
ethane	1-octene	0.9699 – 1.0550	1.4488 – 2.2951	1.52098 – 1.96829	6	[141]
ethane	1-tetradecene	0.9601 – 1.0550	1.4139 – 2.2951	1.51900 – 1.99246	9	[141]
ethanol	ammonia	0.5802 – 0.6288	0.0896 – 2.2508	2.75882 – 2.87562	18	[40]
ethanol	benzene	0.5414 – 1.0780	–	1.44361 – 2.92132	21	[142-143]
ethanol	benzonitrile	0.5896 – 0.6285	0.2427 – 1.5814	2.76731 – 2.83113	16	[144]
ethanol	benzyl acetate	0.6094 – 0.6483	2.4430 – 5.7003	2.77185 – 2.88603	15	[66]
ethanol	1,2-butanediol	0.5414 – 0.7239	0.0163	2.58066 – 2.92134	5	[143]
ethanol	1,4-butanediol	0.5414 – 0.7239	0.0163	2.58066 – 2.92134	4	[143]
ethanol	1-butanol	0.5414 – 0.7239	0.0163	2.58066 – 2.92134	4	[143]
ethanol	carbon dioxide	0.5802 – 0.6775	0.0700 – 2.5098	2.66053 – 2.88360	27	[40]
ethanol	dibenzyl ether	0.6094 – 0.6483	2.4430 – 5.7003	2.77185 – 2.88603	15	[66]
ethanol	ethylene glycol	0.5414 – 0.7239	0.0163	2.58066 – 2.92134	5	[143]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
ethanol	glycerol	0.5414 – 0.7239	0.0163	2.58066 – 2.92134	5	[143]
ethanol	naphthalene	0.7262 – 1.0780	–	1.44361 – 2.59705	13	[142]
ethanol	nitrous oxide	0.5801 – 0.6480	0.0163	2.73313 – 2.85583	5	[145]
ethanol	phenanthrene	0.9212 – 1.0780	–	1.44361 – 2.05660	13	[142]
ethanol	2-phenylethyl acetate	0.6094 – 0.6483	2.4430 – 5.7003	2.77185 – 2.88603	15	[66]
ethanol	3-phenylpropyl acetate	0.6094 – 0.6483	2.4430 – 5.7003	2.77185 – 2.88603	15	[66]
ethanol	propane	0.5802 – 0.6775	0.0619 – 2.3176	2.66053 – 2.87671	30	[40]
ethanol	propene	0.5802 – 0.6775	0.0619 – 2.2345	2.66053 – 2.87707	30	[40]
ethanol	toluene	0.7262 – 1.0780	–	1.44361 – 2.59705	14	[142]
ethanol	1,3,5-trimethylbenzene	0.7262 – 1.0780	–	1.44361 – 2.59705	13	[142]
ethanol	water	0.5414 – 0.7262	0.0163	2.57564 – 2.92134	15	[28, 143, 146]
ethylene	carbon dioxide	1.0560 – 1.2330	0.2170 – 3.7240	0.05140 – 1.59350	49	[98]
ethylene	helium	0.9920 – 1.4160	0.0200	0.0040 – 0.00580	7	[31]
ethylene	nitrogen	1.1430 – 1.5930	0.0200	0.00350 – 0.00490	7	[100]
ethylene glycol	propene	0.4622 – 0.5398	0.0458 – 0.9152	3.30283 – 3.42408	31	[123-124]
helium	argon	14.8750 – 155.2990	0.4460 – 26.6920	0.00090 – 0.16310	36	[37, 147-151]
helium	*n*-butane	53.9500 – 139.3060	0.4460	0.00100 – 0.00240	19	[103, 152-154]
helium	1-butanol	81.5030 – 100.7710	0.4460	0.00130 – 0.00170	6	[37, 103]
helium	carbon dioxide	47.7840 – 95.9540	0.4460 – 22.2290	0.00140 – 0.13650	24	[37, 103, 150]
helium	ethane	53.9500 – 139.3060	0.4460	0.00100 – 0.00250	38	[103, 152, 154-156]
helium	ethanol	57.4180 – 100.7710	0.4460	0.00130 – 0.00230	7	[37, 103]
helium	ethylene	53.9500 – 91.8110	0.4460	0.00150 – 0.00250	20	[103, 155-157]
helium	*n*-hexane	57.4180 – 91.1370	0.4460	0.00150 – 0.00230	5	[103, 153]
helium	1-hexanol	81.5030 – 100.7710	0.4460	0.00130 – 0.00170	6	[37, 103]
helium	hydrogen	22.7360 – 176.6860	0.4460	0.00080 – 0.00590	17	[35, 158]
helium	krypton	57.4180 – 230.0960	0.4460	0.00060 – 0.00230	10	[148]
helium	methane	38.5360 – 77.0710	0.4460 – 365.1270	0.00170 – 1.39440	53	[103, 150, 152, 154, 157, 159-162]
helium	methanol	81.5030 – 100.7710	0.446	0.0013 – 0.0017	6	[37, 103]
helium	nitrogen	14.8750 – 155.2990	0.446	0.0009 – 0.1631	34	[37, 103, 147-149, 163]
helium	oxygen	57.4180 – 95.9540	0.446	0.0014 – 0.0023	12	[37, 103, 147-148]
helium	1-pentanol	81.5030 – 100.7710	0.446	0.0013 – 0.0017	6	[37, 103]
helium	propane	57.8040 – 139.3060	0.446	0.0010 – 0.0023	10	[152]
helium	1-propanol	81.5030 – 100.7710	0.446	0.0013 – 0.0017	6	[37, 103]
helium	2-propanol	81.5030 – 100.7710	0.446	0.0013 – 0.0017	6	[37, 103]
helium	propene	56.0690 – 86.5900	0.446	0.0016 – 0.0024	14	[103, 155-157]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
n-heptane	benzene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	11	[164-166]
n-heptane	*n*-decane	0.5518 – 0.8828	0.0365 – 1.2701	2.18248 – 2.92987	6	[138, 167]
n-heptane	*n*-dodecane	0.5518 – 0.8828	0.0365 – 1.2956	2.18248 – 2.94125	6	[138, 167]
n-heptane	ethylbenzene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	4	[166]
n-heptane	*n*-hexadecane	0.5518 – 0.8828	0.0365 – 1.2701	2.12506 – 2.92987	9	[138, 168]
n-heptane	*n*-hexane	0.5238 – 0.6163	0.0370	2.80032 – 2.98470	11	[169-171]
n-heptane	*n*-octane	0.5423 – 0.8828	0.0365 – 1.2701	2.18248 – 2.94858	13	[138, 169, 172]
n-heptane	*n*-tetradecane	0.5518 – 0.8828	0.0365 – 1.2956	2.18248 – 2.94125	6	[138, 167]
n-heptane	toluene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	4	[166]
n-heptane	1,3,5-trimethylbenzene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	4	[166]
n-heptane	2,2,4-trimethylpentane	0.5703 – 0.5981	0.0370	2.83752 – 2.89322	4	[172]
n-heptane	*o*-xylene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	4	[166]
n-heptane	*p*-xylene	0.5612 – 0.6167	0.0370	2.79954 – 2.91141	4	[166]
n-hexadecane	carbon dioxide	0.4476 – 0.7814	0.9908 – 2.4539	2.30516 – 3.10277	10	[137]
n-hexadecane	carbon monoxide	0.4476 – 0.7814	0.9908 – 2.4539	2.30516 – 3.10277	10	[137]
n-hexadecane	*n*-decane	0.4476 – 0.7814	1.0043 – 1.0206	2.36065 – 3.09168	5	[173]
n-hexadecane	*n*-dodecane	0.4476 – 0.7814	1.0043 – 1.0206	2.36065 – 3.09168	5	[173]
n-hexadecane	hydrogen	0.4476 – 0.7814	0.9908 – 2.4539	2.30516 – 3.10277	10	[137]
n-hexadecane	*n*-octane	0.4476 – 0.7814	1.0043 – 2.4858	2.36065 – 3.09496	10	[173]
n-hexadecane	*n*-tetradecane	0.4476 – 0.7814	1.0043 – 1.0206	2.36065 – 3.09168	5	[173]
hexafluoroethane	helium	0.9560 – 1.3660	0.0340	0.00690 – 0.01000	7	[31]
n-hexane	acetone	0.5974 – 0.6566	5.3156 – 8.3056	2.75909 – 2.86591	5	[126]
n-hexane	acetonitrile	0.5876	0.0336 – 128.1063	2.81220 – 3.46738	7	[174]
n-hexane	benzene	0.4201 – 1.0703	[f]	1.34814 – 3.44935	48	[126, 130-131, 174-178]
n-hexane	carbon disulphide	0.5876	0.0336 – 127.5748	2.81220 – 3.46652	10	[174]
n-hexane	carbon tetrabromide	0.5875	0.0332 – 116.2791	2.81793 – 3.44770	8	[179]
n-hexane	*o*-difluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	*p*-difluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	9,10-dimethylanthracene	0.5875	0.0332 – 116.2791	2.81793 – 3.44770	8	[179]
n-hexane	1,1'-dimethylferrocene	0.6170	0.0565 – 6.3189	2.75175 – 2.84213	4	[129]
n-hexane	ethylferrocene	0.6170	0.0532 – 6.3156	2.75167 – 2.84208	4	[129]
n-hexane	ferrocene	0.6170	0.0565 – 6.3189	2.75175 – 2.84213	4	[129]
n-hexane	*n*-heptane	0.5576 – 0.7842	0.0337	2.69817 – 2.87512	11	[169-171, 180]
n-hexane	hexafluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	indole	0.6170	5.3160 – 8.3060	2.79070 – 2.86370	4	[108, 181]
n-hexane	naphthalene	0.5875 – 1.0703	[g]	1.34814 – 2.86372	21	[126, 131, 174, 177]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
n-hexane	octafluorotoluene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	*n*-octane	0.5813 – 0.6463	0.0337	2.69817 – 2.82956	7	[169, 180]
n-hexane	pentafluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	phenanthrene	0.6566 – 1.0703	sat.p[f]; $P_{r,1} > 1$	1.34814 – 2.67052	15	[131]
n-hexane	pyrene	0.5875	0.0332 – 116.2791	2.81793 – 3.44770	8	[177, 179]
n-hexane	1,2,3,5-tetrafluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	1,2,4,5-tetrafluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	toluene	0.5875 – 1.0703	[h]	1.34814 – 3.45922	32	[126, 131, 182-183]
n-hexane	1,2,4-trifluorobenzene	0.4201 – 0.6566	0.0337	2.66876 – 3.13550	7	[178]
n-hexane	1,3,5-trimethylbenzene	0.5974 – 1.0703	[g]	1.34814 – 2.86372	20	[126, 131]
n-hexane	vitamin K_3	0.6171	5.3156 – 8.3056	2.82912 – 2.86591	5	[108, 126]
n-hexane	*m*-xylene	0.5974 – 0.6566	5.3156 – 8.3056	2.75909 – 2.86591	5	[126]
n-hexane	*p*-xylene	0.6171 – 1.0703	[g]	1.34814 – 2.86372	17	[126, 131]
krypton	argon	1.6190 – 5.7080	0.0180	0.00090 – 0.00330	6	[184]
krypton	helium	1.7100 – 5.7030	0.0180	0.00090 – 0.00310	6	[184]
krypton	neon	1.3040 – 5.8380	0.0180	0.00090 – 0.00410	17	[39, 184]
krypton	xenon	1.7130 – 5.3130	0.0180	0.00100 – 0.00310	8	[184]
methane	carbon dioxide	1.5020 – 1.9320	0.0220	0.00330 – 0.00420	10	[185]
methane	tetrachloroethene	1.4870 – 1.8020	0.0220	0.00350 – 0.00430	5	[186]
methanol	acetonitrile	0.5525 – 0.6110	0.0124 – 33.4857	2.83864 – 3.36893	26	[29]
methanol	ammonia	0.5817 – 0.6792	0.0272 – 1.6304	2.69188 – 2.91357	24	[40]
methanol	benzene	0.6110 – 0.9236	–	2.05512 – 2.84555	4	[187]
methanol	carbon dioxide	0.5817 – 0.6792	0.0272 – 1.6304	2.69188 – 2.91357	25	[40]
methanol	carbon monoxide	0.5830 – 0.7085	0.0124	2.66095 – 2.89268	8	[188]
methanol	*p*-chloronitrobenzene	0.6305 – 0.6696	0.4187 – 1.2833	2.74640 – 2.84397	18	[189]
methanol	naphthalene	0.6110 – 0.9236	–	2.05512 – 2.84555	4	[187]
methanol	phenanthrene	0.6110 – 0.9236	–	2.05512 – 2.84555	4	[187]
methanol	propane	0.5817 – 0.6792	0.0272 – 1.6984	2.69188 – 2.91798	27	[40]
methanol	toluene	0.6110 – 0.9236	–	2.05512 – 2.84555	4	[187]
methanol	1,3,5-trimethylbenzene	0.6110 – 0.9236	–	2.05512 – 2.84555	4	[187]
methanol	water	0.5427 – 0.6109	0.0124	2.84516 – 2.95811	5	[190]
methanol	[Bmim][bti][a]	0.5521 – 0.6497	0.0124	2.77574 – 2.94321	11	[30, 191]
methanol	[Emim][bti][b]	0.5521 – 0.6497	0.0124	2.77574 – 2.94321	11	[30, 191]
methanol	[Hmim][bti][c]	0.5521 – 0.6497	0.0124	2.77574 – 2.94321	5	[30]
methanol	[Omim][bti][d]	0.5521 – 0.6497	0.0124	2.77574 – 2.94321	5	[30]
methyl fluoride	helium	0.8890 – 1.2700	0.0180	0.00350 – 0.00500	7	[31]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
neon	deuterium	2.5900 – 6.6440	0.0370	0.00170 – 0.00440	5	[35]
neon	helium	1.7250 – 8.8740	0.0370	0.00130 – 0.00660	24	[35-36, 39]
neon	hydrogen	2.5900 – 6.6440	0.0370	0.00170 – 0.00440	5	[35]
neon	xenon	6.1490 – 8.8740	0.0370	0.00130 – 0.00190	6	[39]
nitrogen	acetone	2.7190 – 3.0370	0.0300	0.00290 – 0.00320	5	[101, 103]
nitrogen	benzene	2.2820 – 3.3530	0.0300	0.00260 – 0.00380	21	[101, 103, 151, 192]
nitrogen	*n*-butane	2.4840 – 5.3190	0.0300	0.00160 – 0.00350	5	[193]
nitrogen	carbon tetrachloride	2.8820 – 3.3530	0.0300	0.00260 – 0.00300	5	[101, 103]
nitrogen	ethane	2.3630 – 5.7290	0.0300	0.00150 – 0.00370	39	[100, 103, 140, 152, 155]
nitrogen	helium	1.5460 – 3.7490	0.0300	0.00230 – 0.00560	48	[33-34, 37, 101, 103, 147]
nitrogen	hydrogen	2.4020 – 3.5910	0.0300	0.00240 – 0.00360	29	[194]
nitrogen	methane	2.4020 – 3.5910	0.0300	0.00240 – 0.00360	29	[194]
nitrogen	propane	2.3200 – 5.7290	0.0300	0.00150 – 0.00370	20	[152, 154, 195]
nitrogen	trichloromethane	2.8610 – 3.3140	0.0300	0.00260 – 0.00300	5	[101, 103]
n-octacosane	carbon dioxide	0.4293 – 0.6179	2.1076	2.64346 – 3.08418	5	[196]
n-octacosane	carbon monoxide	0.4293 – 0.6179	2.1076	2.64346 – 3.08418	5	[196]
n-octacosane	*n*-dodecane	0.4316 – 0.6179	2.1076	2.64346 – 3.07890	5	[196]
n-octacosane	*n*-hexadecane	0.4316 – 0.6179	2.1076	2.64346 – 3.07890	5	[196]
n-octacosane	hydrogen	0.4293 – 0.6179	2.1076	2.64346 – 3.08418	5	[196]
n-octacosane	*n*-octane	0.4316 – 0.6179	2.1076	2.64346 – 3.07890	5	[196]
octafluorocyclobutane	helium	0.7210 – 1.0300	0.0370	0.01010 – 0.01480	7	[31]
octafluoropropane	helium	0.8120 – 1.1590	0.0370	0.00930 – 0.01350	7	[31]
n-octane	argon	0.5239 – 0.7085	0.0407	2.59373 – 3.00798	4	[132]
n-octane	benzene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]
n-octane	carbon tetrachloride	0.5239 – 0.6558	0.0407	2.73785 – 3.00798	4	[132]
n-octane	ethylbenzene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]
n-octane	*n*-heptane	0.5151 – 0.6030	0.0407	2.84905 – 3.02530	7	[169, 198]
n-octane	*n*-hexane	0.5186 – 0.5854	0.0407	2.88502 – 3.01836	6	[169]
n-octane	krypton	0.5239 – 0.7085	0.0407	2.59373 – 3.00798	4	[132]
n-octane	methane	0.5239 – 0.7085	0.0407	2.59373 – 3.00798	4	[132]
n-octane	tetrabutyltin	0.5239 – 0.7613	0.0407	2.49758 – 3.00798	4	[132]
n-octane	tetraethyltin	0.5239 – 0.7613	0.0407	2.49758 – 3.00798	5	[132]
n-octane	tetramethyltin	0.5239 – 0.7613	0.0407	2.49758 – 3.00798	4	[132]
n-octane	tetrapropyltin	0.5239 – 0.7613	0.0407	2.49758 – 3.00798	4	[132]
n-octane	1,3,5-trimethylbenzene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
n-octane	toluene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]
n-octane	xenon	0.4978 – 0.7085	0.0407	2.59373 – 3.05929	8	[132, 134]
n-octane	*o*-xylene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]
n-octane	*p*-xylene	0.5331 – 0.5858	0.0407	2.88428 – 2.98994	8	[166, 197]
oxygen	helium	1.9290 – 3.2220	0.0200	0.00180 – 0.00300	8	[37]
oxygen	hydrogen	1.9610 – 2.9310	0.0200	0.00200 – 0.00300	13	[194]
propane	helium	0.7570 – 1.0820	0.0240	0.00630 – 0.00910	7	[31]
propane	1-octene	0.8018 – 0.9127	1.3082 – 2.1976	2.02963 – 2.37289	8	[141]
propane	1-tetradecene	0.7910 – 0.9124	2.0918 – 2.1647	2.10279 – 2.39596	8	[141]
1-propanol	ammonia	0.5554 – 0.6486	0.2031 – 3.2128	2.74880 – 2.94303	31	[40]
1-propanol	carbon dioxide	0.5554 – 0.6486	0.1644 – 3.5068	2.75681 – 2.94850	27	[40]
1-propanol	propane	0.5554 – 0.6486	0.1644 – 3.0619	2.74880 – 2.94048	36	[40]
1-propanol	propene	0.5554 – 0.6486	0.1644 – 3.2611	2.74880 – 2.94412	36	[40]
1-propanol	water	0.5554 – 0.6299	0.0193	2.78657 – 2.92237	5	[199]
2-propanol	benzene	0.7342 – 1.0545	–	1.52656 – 2.59185	10	[187]
2-propanol	*n*-decane	0.6555 – 1.0545	–	1.52656 – 2.74561	10	[187]
2-propanol	naphthalene	0.7342 – 1.0545	–	1.52656 – 2.59185	10	[187]
2-propanol	phenanthrene	0.7342 – 1.0545	–	1.52656 – 2.59185	9	[187]
2-propanol	*n*-tetradecane	0.7342 – 1.0545	–	1.52656 – 2.59185	9	[187]
2-propanol	toluene	0.7342 – 1.0545	–	1.52656 – 2.59185	10	[187]
2-propanol	water	0.5866 – 0.6653	0.0210	2.71558 – 2.86517	5	[199]
propene	helium	0.7670 – 1.0960	0.0220	0.00560 – 0.00810	7	[31]
sulfur hexafluoride	benzene	1.0292	0.9310 – 3.8160	0.40834 – 1.90560	9	[125]
sulfur hexafluoride	benzoic acid	1.0298 – 1.0612	1.7287 – 3.1915	1.24846 – 1.90649	6	[114]
sulfur hexafluoride	carbon tetrachloride	1.0292	1.1170 – 3.8160	0.68057 – 1.90560	6	[125]
sulfur hexafluoride	cyclohexane	0.8880 – 1.0770	0.0270	0.00710 – 0.00860	5	[200]
sulfur hexafluoride	methylcyclohexane	0.8880 – 1.0770	0.0270	0.00710 – 0.00860	5	[200]
sulfur hexafluoride	naphthalene	0.9984 – 1.0298	1.7287 – 3.1915	1.50889 – 2.02776	5	[114]
sulfur hexafluoride	toluene	1.0292	0.9310 – 3.8160	0.40834 – 1.90560	11	[125]
sulfur hexafluoride	1,3,5-trimethylbenzene	1.0292 – 1.0292	1.1170 – 3.8160	0.68057 – 1.90560	10	[125]
sulfur hexafluoride	*p*-xylene	0.8886 – 1.0610	0.7980 – 3.9890	0.40834 – 2.24588	52	[125]
n-tetradecane	acridine	0.4808 – 0.6828	0.0704	2.66637 – 3.07925	8	[201]
n-tetradecane	benzothiophene	0.4808 – 0.6540	0.0704	2.73115 – 3.07925	7	[201]
n-tetradecane	dibenzothiophene	0.4808 – 0.6684	0.0704	2.69900 – 3.07925	8	[201]
n-tetradecane	naphthalene	0.4519 – 0.6540	0.0704	2.73115 – 3.13211	7	[201]
n-tetradecane	xenon	0.4086 – 0.4519	0.0704	3.13224 – 3.20942	4	[134]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
tetrafluoromethane	helium	1.230 – 1.758	0.027	0.0043 – 0.0062	7	[31]
tetrafluoromethane	tetrachloroethene	1.244 – 1.508	0.027	0.0050 – 0.0060	5	[186]
tetrafluoromethane	1,1,1-trichloroethane	1.244 – 1.508	0.027	0.0050 – 0.0060	5	[186]
2,2,4-trimethylpentane	benzene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
2,2,4-trimethylpentane	ethylbenzene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
2,2,4-trimethylpentane	toluene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
2,2,4-trimethylpentane	1,3,5-trimethylbenzene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
2,2,4-trimethylpentane	*o*-xylene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
2,2,4-trimethylpentane	*p*-xylene	0.5574 – 0.6125	0.0394	2.70609 – 2.81142	4	[197]
water	acetamide	0.4282 – 0.4791	0.0045	3.14846 – 3.16950	4	[202]
water	acetone	0.4606 – 0.5070	0.0045	3.12428 – 3.16022	4	[28]
water	alanine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	alloisoleucine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	allothreonine	0.4530 – 0.5148	0.0045	3.11628 – 3.16386	6	[204]
water	aluminium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	ammonia	0.4526 – 0.5144	0.0045	3.11661 – 3.16399	5	[206]
water	arabinose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[207]
water	argon	0.4221 – 0.4758	0.0045	3.15085 – 3.16948	8	[208]
water	barium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	benzene	0.4251 – 0.5747	0.0045	3.04019 – 3.16947	24	[209-212]
water	benzoic acid	0.4374 – 0.5224	0.0045	3.10798 – 3.16863	12	[213]
water	beryllium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	biphenyl	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	7	[209]
water	*n*-butane	0.4282 – 0.5147	0.0045	3.11636 – 3.16950	16	[210, 214-215]
water	1,2-butanediol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	1,3-butanediol	0.4604 – 0.5376	0.0045	3.09017 – 3.16034	5	[216]
water	1,4-butanediol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	1-butanol	0.4282 – 0.5747	0.0045	3.04019 – 3.16950	13	[202, 217-218]
water	2-methyl-1-butanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	3-methyl-1-butanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	2-methyl-2-butanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	3-methyl-2-butanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	*n*-butylbenzene	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	7	[209]
water	α-amino-*n*-butyric acid	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	caffeine	0.4529 – 0.5224	0.0045	3.10798 – 3.16389	22	[220-222]
water	calcium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]

Table 3.1 (*Continued*)

System		$T_{\mathrm{r},1}$	$P_{\mathrm{r},1}$	$\rho_{\mathrm{r},1}$	NDP	Data Sources
Solvent (1)	Solute (2)					
water	camphor	0.4374 – 0.4915	0.0045	3.13859 – 3.16863	8	[213]
water	carbon dioxide	0.4221 – 0.5685	0.0045	3.04913 – 3.16948	111	[206, 208, 214-215, 223-246]
water	cesium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[247]
water	cinnamic acid	0.4374 – 0.4915	0.0045	3.13859 – 3.16863	8	[213]
water	α-cyclodextrin	0.4606 – 0.4822	0.0045	3.14613 – 3.16022	4	[248]
water	β-cyclodextrin	0.4606 – 0.4822	0.0045	3.14613 – 3.16022	4	[249]
water	cyclohexane	0.4251 – 0.5147	0.0045	3.11636 – 3.16940	10	[210-211]
water	cyclopentane	0.4251 – 0.5147	0.0045	3.11636 – 3.16940	10	[210-211]
water	diethanolamine	0.4604 – 0.5376	0.0046	3.08907 – 3.16039	5	[250]
water	diethylene glycol	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[251]
water	*N*,*N*-diethylethanolamine	0.4683 – 0.5301	0.0045	3.09161 – 3.15088	5	[252-253]
water	diglycolamine	0.4683 – 0.5301	0.0045	3.09915 – 3.15580	5	[254]
water	diisopropanolamine	0.4604 – 0.5376	0.0046	3.09034 – 3.15944	5	[250]
water	dimethylethanolamine	0.4683 – 0.5301	0.0045	3.09161 – 3.15088	5	[252-253]
water	dipropylene glycol	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[255]
water	*meso*-erythritol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	ethane	0.4282 – 0.5147	0.0045	3.11636 – 3.16950	16	[210, 214, 256]
water	ethanol	0.4413 – 0.5747	0.0045	3.04019 – 3.16781	22	[28, 146, 202, 217-218]
water	ethylbenzene	0.4251 – 0.5688	0.0050	3.04871 – 3.16942	16	[210-212]
water	ethylene glycol	0.4607 – 0.5457	0.0045	3.08011 – 3.16018	9	[218, 251]
water	1-ethylnaphthalene	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	7	[209]
water	formamide	0.4282 – 0.4791	0.0045	3.14846 – 3.16950	4	[202]
water	fructose	0.4606 – 0.4822	0.0045	3.14613 – 3.16022	4	[257]
water	furfural	0.4607 – 0.5457	0.0045	3.08011 – 3.16018	7	[258]
water	5-(hydroxymethyl) furfural	0.4607 – 0.5457	0.0045	3.08011 – 3.16018	7	[258]
water	galactose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[207]
water	gallium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	glucose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	10	[207, 257]
water	glycerol	0.4298 – 0.5457	0.0045	3.08011 – 3.16947	10	[216, 218]
water	glycine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	guaiacol	0.4607 – 0.5457	0.0045	3.08011 – 3.16018	7	[258]
water	hexafluorobenzene	0.4607 – 0.5688	0.0045	3.04869 – 3.16018	6	[212]
water	1,2,6-hexanetriol	0.4604 – 0.5376	0.0045	3.09017 – 3.16034	5	[216]
water	homoserine	0.4530 – 0.5148	0.0045	3.11628 – 3.16386	6	[204]
water	hydrogen	0.4374 – 0.4761	0.0046	3.15069 – 3.16863	6	[235, 259]

Table 3.1 (*Continued*)

System		$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
Solvent (1)	Solute (2)					
water	hydrogen sulfide	0.4452 – 0.5685	0.0045	3.04913 – 3.16673	22	[214, 223, 260]
water	*myo*-inositol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	isobutyramide	0.4282 – 0.4791	0.0045	3.14846 – 3.16950	4	[202]
water	isoleucine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	krypton	0.4374 – 0.4761	0.0046	3.15069 – 3.16863	6	[235, 259]
water	lactose	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[257]
water	leucine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	*tert*-leucine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	lithium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[247]
water	magnesium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	mannitol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	mannose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[207]
water	methane	0.4295 – 0.5296	0.0045	3.09978 – 3.16948	32	[208, 210, 214, 256]
water	methanol	0.4413 – 0.5610	0.0045	3.05965 – 3.16781	15	[190, 202, 261-263]
water	methyl bromide	0.4372 – 0.4758	0.0045	3.15085 – 3.16867	6	[208]
water	methyl chloride	0.4372 – 0.4758	0.0045	3.15085 – 3.16867	6	[208]
water	methylcyclopentane	0.4251 – 0.5147	0.0045	3.11636 – 3.16940	10	[210-211]
water	*n*-methyldiethanolamine	0.4604 – 0.5376	0.0046	3.09034 – 3.15912	5	[250]
water	methyl fluoride	0.4372 – 0.4758	0.0045	3.15085 – 3.16867	6	[208]
water	*N*-methylpyrrolidone	0.4604 – 0.5376	0.0045	3.09017 – 3.16034	5	[216]
water	monoethanolamine	0.4606 – 0.5301	0.0045	3.09161 – 3.15976	9	[250, 252-253]
water	monoisopropanolamine	0.4683 – 0.5301	0.0045	3.09161 – 3.15088	5	[252-253]
water	naphthalene	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	7	[209]
water	2-naphthol	0.4374 – 0.5687	0.0045	3.04880 – 3.16863	16	[213]
water	neon	0.4374 – 0.4761	0.0046	3.15069 – 3.16863	6	[235, 259]
water	nitrous oxide	0.4449 – 0.5687	0.0045	3.04880 – 3.16680	78	[223-224, 263]
water	norleucine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	norvaline	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	oxygen	0.4362 – 0.5687	0.0045	3.04880 – 3.16884	34	[135, 264]
water	pentaerythritol	0.4298 – 0.5750	0.0045	3.03974 – 3.16947	6	[218]
water	*n*-pentane	0.4282 – 0.5147	0.0045	3.11636 – 3.16950	8	[210, 214]
water	2-methyl-2,4-pentanediol	0.4604 – 0.5376	0.0045	3.09017 – 3.16034	5	[216]
water	1-pentanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	2-pentanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	3-pentanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	phenol	0.4607 – 1.0017	0.0045 – 1.3629	1.76814 – 3.19462	17	[258, 265]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
water	piperazine	0.4683 – 0.5301	0.0045	3.09161 – 3.15088	5	[252-253]
water	2-piperidineethanol	0.4683 – 0.5301	0.0045	3.09915 – 3.15580	5	[254]
water	poly(ethylene glycol) 200	0.4681 – 0.4913	0.0046	3.13879 – 3.15594	4	[266]
water	poly(ethylene glycol) 300	0.4681 – 0.4913	0.0046	3.13879 – 3.15594	4	[266]
water	poly(ethylene glycol) 400	0.4681 – 0.4913	0.0046	3.13879 – 3.15594	4	[266]
water	poly(ethylene glycol) 600	0.4681 – 0.4913	0.0046	3.13879 – 3.15594	4	[266]
water	poly(propylene glycol) 400	0.4681 – 0.4913	0.0046	3.13879 – 3.15594	4	[266]
water	potassium chloride	0.4604 – 0.6537	0.0045 – 3.0995	2.91120 – 3.24453	30	[247, 267]
water	propanamide	0.4282 – 0.4791	0.0045	3.14846 – 3.16950	4	[202]
water	propane	0.4282 – 0.5147	0.0045	3.11636 – 3.16950	16	[210, 214, 256]
water	1-propanol	0.4282 – 0.5747	0.0045	3.04019 – 3.16950	15	[199, 202, 218]
water	2,2-dimethyl-1-propanol	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[219]
water	2-amino-2-methyl-1--propanol	0.4683 – 0.5301	0.0045	3.09915 – 3.15580	5	[254]
water	2-propanol	0.4282 – 0.5471	0.0045	3.07822 – 3.16950	12	[199, 202, 261]
water	2-methyl-2-propanol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	9	[218]
water	propylene glycol	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[255]
water	radon	0.4374 – 0.4761	0.0046	3.15069 – 3.16863	6	[235]
water	rubidium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[247]
water	salicylic acid	0.4374 – 0.5301	0.0045	3.09915 – 3.16863	13	[213]
water	serine	0.4530 – 0.5148	0.0045	3.11628 – 3.16386	6	[204]
water	sodium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[247]
water	strontium chloride	0.4606 – 0.4915	0.0045	3.13859 – 3.16022	5	[205]
water	sucrose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	10	[207, 257]
water	sulfolane	0.4683 – 0.5301	0.0045	3.09161 – 3.15088	5	[252]
water	sulfur dioxide	0.4529 – 0.4761	0.0046	3.15069 – 3.16389	4	[238]
water	tetraethylene glycol	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[251]
water	threonine	0.4530 – 0.5148	0.0045	3.11628 – 3.16386	6	[204]
water	toluene	0.4251 – 0.5688	0.0045	3.04869 – 3.16940	15	[210-212]
water	triethanolamine	0.4683 – 0.5301	0.0045	3.09915 – 3.15580	5	[254]
water	triethylene glycol	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[251]
water	valine	0.4530 – 0.5148	0.0045	3.11633 – 3.16388	6	[203]
water	vanillin	0.4607 – 0.5457	0.0045	3.08011 – 3.16018	7	[258]
water	xenon	0.4374 – 0.4761	0.0046	3.15069 – 3.16863	6	[235, 259]
water	xylitol	0.4298 – 0.5755	0.0045	3.03906 – 3.16947	5	[143]
water	xylose	0.4221 – 0.5457	0.0045	3.08011 – 3.16910	6	[207]
water	[Bmim][BF$_4$]^i	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	11	[30, 268]

Table 3.1 (*Continued*)

System						
Solvent (1)	Solute (2)	$T_{r,1}$	$P_{r,1}$	$\rho_{r,1}$	NDP	Data Sources
water	[Bmim][bti][a]	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	18	[30, 191, 269]
water	[Bmim][CF_3SO_3][j]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[268]
water	[Bmim][Cl][k]	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	6	[30]
water	[Bmim][$MeSO_4$][l]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[268]
water	[Bmim][$OcSO_4$][m]	0.4452 – 0.4838	0.0045	3.14493 – 3.16673	6	[269]
water	[Bmim][PF_6][n]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[268]
water	[Emim][BF_4][o]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[270]
water	[Emim][bti][b]	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	18	[30, 191, 269]
water	[Emim][$C_2H_5SO_4$][p]	0.4452 – 0.4993	0.0045	3.13162 – 3.16673	11	[269-270]
water	[Emim][C_2N_3][q]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[270]
water	[Emim][CF_3SO_3][r]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[270]
water	[Emim][$MDEGSO_4$][s]	0.4684 – 0.4993	0.0045	3.13162 – 3.15575	5	[270]
water	[Hmim][bti][c]	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	6	[30]
water	[Omim][bti][d]	0.4372 – 0.5144	0.0045	3.11661 – 3.16867	6	[30]

[a] 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [b] 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [c] 1-hexyl-3-methyl--imidazolium bis[(trifluoromethyl)sulfonyl]imide; [d] 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide; [e] sat.p. : saturation pressure; [f] $P_{r,1}$ from 0.034 to 122.69 and at saturation pressure; [g] $P_{r,1}$ = 0.498 and 0.532, at saturation pressure and other points at $P_{r,1}$ >1; [h] $P_{r,1}$ from 0.034 to 124.58 and saturation pressure; [i] 1-butyl-3-methylimidazolium tetrafluoroburate; [j] 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [k] 1-butyl-3-methylimidazolium chloride; [l] 1-butyl-3-methylimidazolium methylsulfate; [m] 1-butyl-3-methylimidazolium octylsulfate; [n] 1-butyl-3-methylimidazolium hexafluorophosphate; [o] 1-ethyl-3--methylimidazolium tetrafluoroburate; [p] 1-ethyl-3-methylimidazolium ethylsulfate; [q] 1-ethyl-3-methylimidazolium dicyanamide; [r] 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; [s] 1-ethyl-3-methylimidazolium diethylene glycol monomethyl ether sulfate. Note: An hyphen means that data is not available.

Table 3.2. Data and properties of pure substances involved in database of tracer diffusivities (Table 3.1): name, formula, CAS number, critical constants (T_c, P_c and V_c), and molar volume at its normal boiling point (V_bp).

Substance	Formula	CAS Number	M ($\mathrm{g \cdot mol^{-1}}$)	T_c (K)	P_c (bar)	V_c ($\mathrm{cm^3 \cdot mol^{-1}}$)	V_bp [o] ($\mathrm{cm^3 \cdot mol^{-1}}$)
acetamide	C_2H_5NO	60-35-5	59.07	761.00[a]	66.00[a]	215.00[a]	79.29
acetone	C_3H_6O	67-64-1	58.08	508.10[b]	47.00[b]	209.00[b]	76.98
acetonitrile	C_2H_3N	75-05-8	41.05	545.50[b]	48.30[b]	173.00[b]	63.14
acetylene	C_2H_2	74-86-2	26.04	308.30[b]	61.14[b]	112.20[b]	40.11
acridine	$C_{13}H_9N$	260-94-6	179.22	905.00[c]	36.40[c]	543.00[c]	209.37
adamantanone	$C_{10}H_{14}O$	700-58-3	150.22	759.15[d]	31.55[d]	368.22[d]	139.36
alanine	$C_3H_7NO_2$	302-72-7	89.09	698.48[e]	54.71[e]	205.50[e]	75.63
alloisoleucine	$C_6H_{13}NO_2$	3107-04-8	131.17	762.89[e]	35.14[e]	411.00[e]	156.37
allothreonine	$C_4H_9NO_3$	144-98-9	119.12	827.59[e]	52.31[e]	316.90[e]	119.07
aluminium chloride	$AlCl_3$	7446-70-0	133.34	–	–	–	–
allylbenzene	C_9H_{10}	300-57-2	118.18	639.86[f]	33.50[f]	419.80[f]	159.88
ammonia	NH_3	7664-41-7	17.03	405.50[b]	113.30[b]	72.50[b]	25.38
aniline	C_6H_7N	62-53-3	93.13	699.00[b]	53.10[b]	274.00[b]	102.24
anisole	C_7H_8O	100-66-3	108.14	641.65[a]	41.75[a]	337.00[a]	127.00
anthracene	$C_{14}H_{10}$	120-12-7	178.23	873.00[a]	29.00[a]	554.00[a]	213.82
arabinose	$C_5H_{10}O_5$	10323-20-3	150.13	1021.42[e]	76.35[e]	370.95[e]	140.44
arachidonic acid (AA)	$C_{20}H_{32}O_2$	506-32-1	304.47	1013.42[e]	12.74[e]	1093.20[e]	435.92
AA ethyl ester	$C_{22}H_{36}O_2$	1808-26-0	332.53	960.63[g]	11.31[g]	1195.26[g]	478.66
argon	Ar	7440-37-1	39.95	150.80[b]	48.70[b]	74.90[b]	26.26
barium chloride	$BaCl_2$	10361-37-2	208.23	–	–	–	–
behenic acid ethyl ester	$C_{24}H_{48}O_2$	5908-87-2	368.64	984.94[g]	9.15[g]	1394.66[g]	562.66
benzene	C_6H_6	71-43-2	78.11	562.20[b]	48.90[b]	259.00[b]	96.38
benzoic acid	$C_7H_6O_2$	65-85-0	122.12	752.00[b]	45.60[b]	341.00[b]	128.58
benzonitrile	C_7H_5N	100-47-0	103.12	699.35[a]	42.15[a]	339.00[a]	127.79
benzothiophene	C_8H_6S	95-15-8	134.20	764.00[h]	47.60[h]	379.00[h]	143.63
benzyl acetate	C9H10O2	140-11-4	150.18	699.00[a]	31.80[a]	449.00[a]	171.55
benzylacetone	$C_{10}H_{12}O$	2550-26-7	148.20	722.51[f]	31.20[f]	500.50[f]	192.23
beryllium chloride	$BeCl_2$	7787-47-5	79.92	–	–	–	–
biphenyl	$C_{12}H_{10}$	92-52-4	154.21	789.00[b]	38.50[b]	502.00[b]	192.83
2-bromoanisole	C_7H_7BrO	578-57-4	187.04	737.58[f]	40.04[f]	378.05[f]	143.26
bromobenzene	C_6H_5Br	108-86-1	157.01	670.00[b]	45.20[b]	324.00[b]	121.87
1,3-butadiene	C_4H_6	106-99-0	54.09[a]	425.00[a]	43.20[a]	221.00[a]	81.61
i-butane	C_4H_{10}	75-28-5	58.12[b]	408.20[b]	36.50[b]	263.00[b]	97.94
n-butane	C_4H_{10}	106-97-8	58.12	425.20[b]	38.00[b]	255.00[b]	94.82
1,2-butanediol	$C_4H_{10}O_2$	584-03-2	90.12	622.14[a]	50.30[a]	291.50[a]	109.09

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M (g·mol^{-1})	T_c (K)	P_c (bar)	V_c (cm^3·mol^{-1})	$V_{bp}{}^{o}$ (cm^3·mol^{-1})
1,3-butanediol	$C_4H_{10}O_2$	107-88-0	90.12	643.00^a	50.00^a	292.00^a	109.29
1,4-butanediol	$C_4H_{10}O_2$	110-63-4	90.12	667.00^a	48.80^a	297.00^a	111.25
1-butanol	$C_4H_{10}O$	71-36-3	74.12	563.10^b	44.20^b	275.00^b	102.63
2-methyl-1-butanol	$C_5H_{12}O$	137-32-6	88.15	565.00^a	38.80^a	327.00^a	123.05
3-methyl-1-butanol	$C_5H_{12}O$	123-51-3	88.15	579.45^a	38.80^a	327.00^a	123.05
2-methyl-2-butanol	$C_5H_{12}O$	75-85-4	88.15	545.15^a	38.80^a	327.00^a	123.05
3-methyl-2-butanol	$C_5H_{12}O$	598-75-4	88.15	574.00^a	39.60^a	327.00^a	123.05
2-butanone	C_4H_8O	78-93-3	72.11	536.80^b	42.10^b	267.00^b	99.50
N-(4-methoxybenzylidene)-4-*n*-butylaniline	$C_{18}H_{21}NO$	26227-73-6	267.37	962.06^d	21.33^d	592.93^d	229.59
n-butylbenzene	$C_{10}H_{14}$	104-51-8	134.22	660.50^b	28.90^b	497.00^b	190.82
tert-butylbenzene	$C_{10}H_{14}$	98-06-6	134.22	660.00^b	29.60^b	492.00^a	188.81
α-amino-*n*-butyric acid	$C_4H_9NO_2$	2835-81-6	103.12	719.32^e	45.14^e	306.90^e	115.14
butyric acid ethyl ester	$C_6H_{12}O_2$	105-54-4	116.20	579.00^i	31.40^i	400.00^i	151.99
caffeine	$C_8H_{10}N_4O_2$	58-08-2	194.20	855.60^i	41.50^i	488.00^i	187.20
calcium chloride	$CaCl_2$	10043-52-4	110.98	–	–	–	–
camphor	$C_{10}H_{16}O$	76-22-2	152.24	709.00^a	29.90^a	460.00^a	175.96
capric acid ethyl ester	$C_{12}H_{24}O_2$	110-38-3	200.00	699.30^i	17.88^i	733.50^i	286.94
caprylic acid ethyl ester	$C_{10}H_{20}O_2$	106-32-1	172.30	655.70^i	21.18^i	621.50^i	241.20
carbon dioxide	CO_2	124-38-9	44.01	304.10^b	73.80^b	93.90^b	33.28
carbon disulphide	CS_2	75-15-0	76.13	552.00^b	79.00^b	160.00^b	58.18
carbon monoxide	CO	630-08-0	28.01	132.90^b	35.00^b	93.20^b	33.02
carbon tetrabromide	CBr_4	558-13-4	331.63	724.91^a	96.31^a	328.50^a	123.64
carbon tetrachloride	CCl_4	56-23-5	153.82	556.40^b	45.60^b	275.90^b	102.98
β-carotene	$C_{40}H_{56}$	7235-40-7	536.88	1450.76^e	6.90^e	1934.95^e	793.00
L-carvone	$C_{10}H_{14}O$	6485-40-1	150.22	709.40^j	26.30^j	504.65^j	193.90
cesium chloride	$CsCl$	7647-17-8	168.36	–	–	–	–
chlorobenzene	C_6H_5Cl	108-90-7	112.56	632.40^b	45.20^b	308.00^b	115.57
chlorotrifluoromethane	$CClF_3$	75-72-9	104.46	302.00^b	38.70^b	180.40^b	65.98
chrysene	$C_{18}H_{12}$	218-01-9	228.29	979.00^a	23.90^a	690.00^a	269.13
cinnamic acid	$C_9H_8O_2$	140-10-3	148.16	797.00^c	35.40^c	446.00^c	170.35
citral	$C_{10}H_{16}O$	5392-40-5	152.24	692.70^e	23.15^e	591.00^e	228.81
p-chloronitrobenzene	$C_6H_4ClNO_2$	100-00-5	157.56	751.00^a	39.80^a	432.00^a	164.75
cobalt(III) acetylacetonate	$C_{15}H_{21}CoO_6$	21679-46-9	356.26	573.48^d	2.52^d	640.95^d	249.11
copper(II) trifluoroacetylacetonate	$C_{10}H_8CuF_6O_4$	14324-82-4	369.70	412.85^d	20.63^d	441.13^d	168.40
12-crown-4	$C_8H_{16}O_4$	294-93-9	176.21	780.66^e	33.59^e	444.75^e	169.85
15-crown-5	$C_{10}H_{20}O_5$	33100-27-5	220.27	876.80^e	28.72^e	548.75^e	211.69

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M ($\mathrm{g \cdot mol^{-1}}$)	T_c (K)	P_c (bar)	V_c ($\mathrm{cm^3 \cdot mol^{-1}}$)	V_{bp}^{o} ($\mathrm{cm^3 \cdot mol^{-1}}$)
18-crown-6	$C_{12}H_{24}O_6$	17455-13-9	264.32	970.51[e]	24.95[e]	652.75[e]	253.92
dicyclohexano-18-crown-6	$C_{20}H_{36}O_6$	16069-36-6	372.50	1177.47[e]	16.24[e]	1002.75[e]	398.19
dibenzo-24-crown-8	$C_{24}H_{32}O_8$	14174-09-5	448.51	1396.77[e]	15.80[e]	1174.35[e]	469.89
dicyclohexano-24-crown-8	$C_{24}H_{44}O_8$	17455-23-1	460.61	1357.66[e]	13.48[e]	1210.75[e]	485.16
α-cyclodextrin	$C_{36}H_{60}O_{30}$	10016-20-3	972.84	2580.29[d]	7.38[d]	1794.01[d]	732.58
β-cyclodextrin	$C_{42}H_{70}O_{35}$	7585-39-9	1134.98	2790.00[d]	6.38[d]	2089.68[d]	859.58
cycloheptanone	$C_7H_{12}O$	502-42-1	112.17	671.19[d]	36.86[d]	297.87[d]	111.59
cyclohexane	C_6H_{12}	110-82-7	84.16	553.50[b]	40.70[b]	308.00[b]	115.57
cyclononanone	$C_9H_{16}O$	3350-30-9	140.22	702.10[d]	31.47[d]	380.74[d]	144.33
cyclopentane	C_5H_{10}	287-92-3	70.14	511.70[b]	45.10[b]	260.00[b]	96.77
cyclopentanone	C_5H_8O	120-92-3	84.12	626.00[a]	58.50[a]	258.00[a]	95.99
n-decane	$C_{10}H_{22}$	124-18-5	142.29	617.70[b]	21.20[b]	603.00[b]	233.68
deuterium	D_2	7782-39-0	4.03[b]	38.40[b]	16.50[b]	60.30[b]	20.92
deuterium oxide	D_2O	7789-20-0	20.03	643.89[b]	216.71[b]	56.26[b]	19.46
dibenzothiophene	$C_{12}H_8S$	132-65-0	184.26	897.00[h]	38.60[h]	512.00[h]	196.86
dibenzyl ether	$C_{14}H_{14}O$	103-50-4	198.27	777.00[a]	25.60[a]	608.00[a]	235.71
1,3-dibromobenzene	$C_6H_4Br_2$	108-36-1	235.91	761.00[a]	46.60[a]	372.00[a]	140.86
1,2-dichlorobenzene	$C_6H_4Cl_2$	95-50-1	147.00	729.00[b]	41.00[b]	360.00[b]	136.10
1,3-dichlorobenzene	$C_6H_4Cl_2$	541-73-1	147.00	683.95[a]	40.70[a]	351.00[a]	132.53
p-dichlorobenzene	$C_6H_4Cl_2$	106-46-7	147.00	684.75[a]	40.70[a]	351.00[a]	132.53
diethanolamine	$C_4H_{11}NO_2$	111-42-2	105.14	736.60[h]	42.70[h]	349.00[h]	131.74
diethylene glycol	$C_4H_{10}O_3$	111-46-6	106.12	744.60[a]	46.00[a]	312.00[a]	117.14
N,*N*-diethylethanolamine	$C_6H_{15}NO$	100-37-8	117.19	592.00[c]	31.80[c]	401.00[c]	152.38
diethyl ether	$C_4H_{10}O$	60-29-7	74.12	466.70[b]	36.40[b]	280.00[b]	104.58
1,2-diethylbenzene	$C_{10}H_{14}$	135-01-3	134.22	668.00[a]	28.80[a]	502.00[a]	192.83
1,4-diethylbenzene	$C_{10}H_{14}$	105-05-5	134.22	657.96[a]	28.03[a]	497.00[a]	190.82
o-difluorobenzene	$C_6H_4F_2$	367-11-3	114.09	554.46[a]	40.67[a]	299.50[a]	112.23
p-difluorobenzene	$C_6H_4F_2$	540-36-3	114.09	556.00[a]	44.00[a]	299.50[a]	112.23
diglycolamine	$C_4H_{11}NO_2$	929-06-6	105.14	699.00[a]	43.60[a]	330.00[a]	124.24
diisopropanolamine	$C_6H_{15}NO_2$	110-97-4	133.19	672.00[h]	36.00[h]	454.00[h]	173.56
diisopropyl ether	$C_6H_{14}O$	108-20-3	102.18	500.30[b]	28.80[b]	386.00[b]	146.42
2,3-dimethylaniline	$C_8H_{11}N$	87-59-2	121.18	717.00[f]	36.30[f]	400.38[f]	152.14
2,6-dimethylaniline	$C_8H_{11}N$	87-62-7	121.18	722.00[k]	42.00[k]	400.38[f]	152.14
9,10-dimethylanthracene	$C_{16}H_{14}$	781-43-1	206.29	899.22[e]	26.27[e]	724.55[e]	283.27
2,3-dimethylbutane	C_6H_{14}	79-29-8	86.18	500.00[b]	31.30[b]	358.00[b]	135.31
dimethylethanolamine	$C_4H_{11}NO$	108-01-0	89.14	571.82[a]	41.40[a]	300.00[a]	112.43

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M $(\mathrm{g \cdot mol^{-1}})$	T_c (K)	P_c (bar)	V_c $(\mathrm{cm^3 \cdot mol^{-1}})$	$V_{\mathrm{bp}}^{\mathrm{o}}$ $(\mathrm{cm^3 \cdot mol^{-1}})$
1,1'-dimethylferrocene	$C_{12}H_{14}Fe$	1291-47-0	214.09	514.45[d]	27.41[d]	400.64[d]	152.24
2,6-dimethylnaphthalene	$C_{12}H_{12}$	581-42-0	156.23	777.00[a]	31.70[a]	520.00[a]	200.09
2,7-dimethylnaphthalene	$C_{12}H_{12}$	582-16-1	156.23	778.00[a]	31.70[a]	520.00[a]	200.09
2,4-dimethylphenol	$C_8H_{10}O$	105-67-9	122.17	707.60[b]	44.00[a]	390.00[a]	148.01
diolein	$C_{39}H_{72}O_5$	2465-32-9	621.99	1025.00[c]	7.92[c]	2150.00[c]	885.61
dipropylene glycol	$C_6H_{14}O_3$	25265-71-8	134.18	654.00[a]	35.80[a]	415.00[a]	157.96
1,3-divinylbenzene	$C_{10}H_{10}$	108-57-6	130.19	692.00[a]	31.20[a]	440.00[a]	167.95
docosahexaenoic acid (DHA)	$C_{22}H_{32}O_2$	6217-54-5	328.49	1075.45[g]	12.41[g]	1148.05[g]	458.86
DHA ethyl ester	$C_{24}H_{36}O_2$	84494-72-4	356.55	1023.28[g]	10.84[g]	1262.06[g]	506.73
DHA methyl ester	$C_{23}H_{34}O_2$	2566-90-7	342.52	999.34[g]	11.41[g]	1206.56[g]	483.40
n-dodecane	$C_{12}H_{26}$	112-40-3	170.34	658.20[b]	18.20[b]	713.00[b]	278.54
n-eicosane	$C_{20}H_{42}$	112-95-8	282.56	767.00[b]	11.10[b]	1190.00[a]	476.45
eicosapentaenoic acid (EPA)	$C_{20}H_{30}O_2$	10417-94-4	302.46	1020.90[g]	13.47[g]	1059.15[g]	421.70
EPA ethyl ester	$C_{22}H_{34}O_2$	73310-10-8	330.51	968.16[g]	11.67[g]	1173.16[g]	469.39
EPA methyl ester	$C_{21}H_{32}O_2$	2734-47-6	316.48	890.55[g]	11.90[g]	1187.03[g]	475.20
meso-erythritol	$C_4H_{10}O_4$	149-32-6	122.12	940.29[e]	79.63[e]	313.95[e]	117.91
ethane	C_2H_6	74-84-0	30.07	305.40[b]	48.80[b]	148.30[b]	53.73
ethanol	C_2H_6O	64-17-5	46.07	513.90[b]	61.40[b]	167.10[b]	60.89
ethyl acetate	$C_4H_8O_2$	141-78-6	88.11	523.20[b]	38.30[b]	286.00[b]	106.93
ethylbenzene	C_8H_{10}	100-41-4	106.17	617.20[b]	36.00[b]	374.00[b]	141.65
ethyl benzoate	$C_9H_{10}O_2$	93-89-0	150.18	668.70[b]	23.20[b]	489.00[a]	187.60
ethylene	C_2H_4	74-85-1	28.05	282.40[b]	50.40[b]	130.40[b]	46.95
ethylene glycol	$C_2H_6O_2$	107-21-1	62.07	645.00[a]	75.30[a]	191.00[a]	70.04
ethylferrocene	$C_{12}H_{14}Fe$	1273-89-8	214.08	554.21[d]	27.41[d]	400.64[d]	152.24
1-ethylnaphthalene	$C_{12}H_{12}$	1127-76-0	156.23	776.00[a]	30.00[a]	520.00[a]	200.09
2-ethyltoluene	C_9H_{12}	611-14-3	120.20	651.00[b]	30.40[b]	460.00[b]	175.96
3-ethyltoluene	C_9H_{12}	620-14-4	120.20	637.00[b]	28.40[b]	490.00[b]	188.01
4-ethyltoluene	C_9H_{12}	622-96-8	120.20	640.00[b]	29.40[b]	470.00[b]	179.97
eucalyptol	$C_{10}H_{18}O$	470-82-6	154.25	698.48[e]	29.54[e]	509.50[e]	195.85
eugenol	$C_{10}H_{12}O_2$	97-53-0	164.20	735.31[f]	33.52[f]	447.23[f]	170.84
ferrocene	$C_{10}H_{10}Fe$	102-54-5	186.04	786.27[d]	32.07[d]	317.77[d]	119.42
2-fluoroanisole	C_7H_7FO	321-28-8	126.13	644.81[f]	38.11[f]	328.87[f]	123.79
fluorobenzene	C_6H_5F	462-06-6	96.10	560.10[b]	45.50[b]	269.00[b]	100.28
3-fluorophenol	C_6H_5FO	372-20-3	112.10	665.54[e]	54.83[e]	339.60[e]	128.03
formamide	CH_3NO	75-12-7	45.04	771.00[a]	78.00[a]	163.00[a]	59.32
fructose	$C_6H_{12}O_6$	57-48-7	180.16	1242.06[d]	30.96[d]	357.45[d]	135.09
furfural	$C_5H_4O_2$	98-01-1	96.08	670.15[h]	56.60[h]	252.00[h]	93.65

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M (g·mol^{-1})	T_c (K)	P_c (bar)	V_c (cm^3·mol^{-1})	V_{bp}^{o} (cm^3·mol^{-1})
5-(hydroxymethyl) furfural	$C_6H_6O_3$	67-47-0	126.11	737.30[h]	49.50[h]	343.00[h]	129.37
galactose	$C_6H_{12}O_6$	59-23-4	180.16	1059.54[h]	67.84[h]	459.00[h]	175.56
gallium chloride	$GaCl_3$	13450-90-3	176.08	–	–	–	–
geraniol	$C_{10}H_{18}O$	106-24-1	154.25	688.44[e]	25.78[e]	571.30[e]	220.82
glucose	$C_6H_{12}O_6$	50-99-7	180.16	755.00[c]	48.20[c]	414.00[c]	157.57
glycerol	$C_3H_8O_3$	56-81-5	92.09	723.00[a]	40.00[a]	264.00[a]	98.33
glycine	$C_2H_5NO_2$	56-40-6	75.07	1021.00[l]	67.40[l]	234.00[l]	86.65
guaiacol	$C_7H_8O_2$	90-05-1	124.14	697.00[h]	47.30[h]	353.00[h]	133.33
helium	He	7440-59-7	4.00	5.19[b]	2.27[b]	57.40[b]	19.87
n-heptane	C_7H_{16}	142-82-5	100.21	540.30[b]	27.40[b]	432.00[b]	164.75
2-heptanone	$C_7H_{14}O$	110-43-0	114.19	611.50[b]	34.40[b]	421.00[a]	160.36
4-heptanone	$C_7H_{14}O$	123-19-3	114.19	595.31[a]	29.96[a]	433.50[a]	165.35
hexachlorobenzene	C_6Cl_6	118-74-1	284.78	825.00[a]	28.50[a]	526.00[a]	202.51
n-hexadecane	$C_{16}H_{34}$	544-76-3	226.45	722.00[b]	14.10[b]	930.00[b]	367.97
1-hexadecene	$C_{16}H_{32}$	629-73-2	224.43	722.00[h]	14.80[h]	933.00[h]	369.22
1,1,1,5,5,5--hexafluoroacetylacetone	$C_5H_2F_6O_2$	1552-22-1	208.06	569.07[g]	27.17[g]	406.05[g]	154.40
hexafluorobenzene	C_6F_6	392-56-3	186.06	516.70[b]	33.00[b]	335.00[b]	126.21
hexafluorobenzene	C_6Cl_6	392-56-3	186.06	516.70[a]	33.00[a]	335.0[a]	126.21
n-hexane	C_6H_{14}	110-54-3	86.18	507.50[b]	30.10[b]	370.00[b]	140.06
1,2,6-hexanetriol	$C_6H_{14}O_3$	106-69-4	134.18	844.91[e]	46.19[e]	415.05[e]	157.98
1-hexanol	$C_6H_{14}O$	111-27-3	102.18	611.35[a]	35.10[a]	381.30[a]	144.55
homoserine	$C_4H_9NO_3$	1927-25-9	119.12	823.94[e]	51.79[e]	323.90[e]	121.83
hydrogen	H_2	1333-74-0	2.02	33.00[b]	12.90[b]	64.30[b]	22.38
hydrogen sulfide	H_2S	7783-06-4	34.08	373.20[b]	89.40[b]	98.60[b]	35.03
indole	C_8H_7N	120-72-9	117.15	790.00[a]	43.00[a]	431.00[a]	164.35
myo-inositol	$C_6H_{12}O_6$	87-89-8	180.16	850.00[c]	53.20[c]	412.00[c]	156.77
iodobenzene	C_6H_5I	591-50-4	204.01	721.00[b]	45.20[b]	351.00[b]	132.53
isobutyramide	C_4H_9NO	563-83-7	87.12	658.00[c]	40.30[c]	321.00[c]	120.69
isoleucine	$C_6H_{13}NO_2$	73-32-5	131.17	761.52[e]	37.55[e]	412.50[e]	156.97
krypton	Kr	7439-90-9	83.80	209.40[b]	55.00[b]	91.20[b]	32.28
lactose	$C_{12}H_{22}O_{11}$	63-42-3	342.30	1431.89[d]	18.77[d]	653.12[d]	254.07
leucine	$C_6H_{13}NO_2$	328-39-2	131.17	761.52[e]	37.55[e]	412.50[e]	156.97
tert-leucine	$C_6H_{13}NO_2$	33105-81-6	131.17	766.89[e]	35.79[e]	404.00[e]	153.58
D-limonene	$C_{10}H_{16}$	5989-27-5	136.24	660.00[a]	27.50[a]	524.00[a]	201.70
linalool	$C_{10}H_{18}O$	78-70-6	154.25	645.80[e]	25.95[e]	558.00[e]	215.44
linoleic acid	$C_{18}H_{32}O_2$	60-33-3	280.45	775.00[c]	14.10[c]	990.00[c]	392.89

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M ($\mathrm{g \cdot mol^{-1}}$)	T_c (K)	P_c (bar)	V_c ($\mathrm{cm^3 \cdot mol^{-1}}$)	V_{bp}^{o} ($\mathrm{cm^3 \cdot mol^{-1}}$)
α-linolenic acid	$C_{18}H_{30}O_2$	463-40-1	278.44	780.00[c]	14.40[c]	1070.00[c]	426.23
γ-linolenic acid	$C_{18}H_{30}O_2$	506-26-3	278.44	958.98[g]	14.17[g]	992.35[g]	393.87
γ-linolenic acid ethyl ester	$C_{20}H_{34}O_2$	1191-41-9	306.48	937.01[d]	17.56[d]	797.37[d]	313.17
linolenic acid methyl ester	$C_{19}H_{32}O_2$	301-00-8	292.46	769.40[h]	13.29[h]	1140.00[h]	455.49
γ-linolenic acid methyl ester	$C_{19}H_{32}O_2$	16326-32-2	292.46	882.79[g]	12.92[g]	1050.86[g]	418.24
lithium chloride	LiCl	7447-41-8	42.39	–	–	–	–
magnesium chloride	$MgCl_2$	7786-30-3	95.21	–	–	–	–
mannitol	$C_6H_{14}O_6$	69-65-8	182.17	1246.06[e]	75.23[e]	445.05[e]	169.97
mannose	$C_6H_{12}O_6$	3458-28-4	180.16	1059.54[h]	67.84[h]	459.00[h]	175.56
methane	CH_4	74-82-8	16.04	190.40[b]	46.00[b]	99.20[b]	35.25
L-menthone	$C_{10}H_{18}O$	14073-97-3	154.25	699.44[j]	25.30[j]	525.24[j]	202.20
methanol	CH_4O	67-56-1	32.04	512.60[b]	80.90[b]	118.00[b]	42.28
2-methylanisole	$C_8H_{10}O$	578-58-5	122.17	648.79[f]	35.60[f]	371.70[f]	140.74
4-methylanisole	$C_8H_{10}O$	104-93-8	122.17	655.36[f]	35.60[f]	371.70[f]	140.74
methyl bromide	CH_3Br	74-83-9	94.94	467.00[a]	80.00[a]	156.00[a]	56.66
methyl chloride	CH_3Cl	74-87-3	50.49	416.30[b]	67.00[b]	138.90[b]	50.16
methylcyclohexane	C_7H_{14}	108-87-2	98.19	572.20[b]	34.70[b]	368.00[b]	139.27
methylcyclopentane	C_6H_{12}	96-37-7	84.16	532.70[b]	37.80[b]	319.00[b]	119.90
n-methyldiethanolamine	$C_5H_{13}NO_2$	105-59-9	119.16	675.00[h]	38.80[h]	368.00[h]	139.27
methyl fluoride	CH_3F	593-53-3	34.03	315.00[b]	56.00[b]	113.20[b]	40.48
1-methylnaphthalene	$C_{11}H_{10}$	90-12-0	142.20	772.00[h]	36.00[h]	465.00[h]	177.97
methyl orange	$C_{14}H_{14}N_3NaO_3S$	547-58-0	327.33	–	–	–	–
N-methylpyrrolidone	C_5H_9NO	872-50-4	99.13	724.00[a]	47.80[a]	316.00[a]	118.72
monoethanolamine	C_2H_7NO	141-43-5	61.08	638.00[a]	68.70[a]	225.00[a]	83.16
monoisopropanolamine	C_3H_9NO	78-96-6	75.11	614.00[a]	56.70[a]	278.00[a]	103.80
monoolein	$C_{21}H_{40}O_4$	111-03-5	356.55	885.00[c]	12.40[c]	1210.00[c]	484.85
myristic acid ethyl ester	$C_{16}H_{32}O_2$	124-06-1	256.43	789.35[g]	13.89[g]	950.66[g]	376.54
myristoleic acid	$C_{14}H_{26}O_2$	544-64-9	226.36	854.23[e]	16.97[e]	819.90[e]	322.45
myristoleic acid methyl ester	$C_{15}H_{28}O_2$	56219-06-8	240.39	777.79[e]	15.26[e]	876.45[e]	345.80
naphthalene	$C_{10}H_8$	91-20-3	128.17	748.40[b]	40.50[b]	413.00[b]	157.17
1-naphthol	$C_{10}H_8O$	90-15-3	144.17	802.00[a]	47.37[a]	375.50[a]	142.24
2-naphthol	$C_{10}H_8O$	135-19-3	144.17	811.40[i]	47.40[i]	375.50[i]	142.24
neon	Ne	7440-01-9	20.18	44.40[b]	27.60[b]	41.60[b]	14.18
2-nitroanisole	$C_7H_7NO_3$	91-23-6	153.14	782.00[a]	37.60[a]	422.00[a]	160.76
nitrobenzene	$C_6H_5NO_2$	98-95-3	123.11	719.00[a]	44.00[a]	349.00[a]	131.74
nitrogen	N_2	7727-37-9	28.01	126.20[b]	33.90[b]	89.80[b]	31.76

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M (g·mol^{-1})	T_c (K)	P_c (bar)	V_c (cm^3·mol^{-1})	V_{bp} ^{o} (cm^3·mol^{-1})
3-nitrotoluene	$C_7H_7NO_2$	99-08-1	137.14	734.00[a]	38.00[a]	441.00[a]	168.35
nitrous oxide	N_2O	10024-97-2	44.01	309.60[b]	72.40[b]	97.40[b]	34.58
n-nonane	C_9H_{20}	111-84-2	128.26	594.60[b]	22.90[b]	548.00[b]	211.39
2-nonanone	$C_9H_{18}O$	821-55-6	142.24	644.29[a]	24.53[a]	545.50[a]	210.38
5-nonanone	$C_9H_{18}O$	502-56-7	142.24	640.00[c]	23.20[c]	560.00[c]	216.24
norleucine	$C_6H_{13}NO_2$	616-06-8	131.17	757.63[e]	37.18[e]	418.50[e]	159.36
norvaline	$C_5H_{11}NO_2$	760-78-1	117.15	737.84[e]	41.95[e]	362.50[e]	137.09
n-octacosane	$C_{28}H_{58}$	630-02-4	394.76	832.00[c]	8.50[c]	1685.60[c]	686.25
octafluorocyclobutane	C_4F_8	115-25-3	200.03	388.37[f]	27.78[f]	324.80[f]	122.19
octafluoropropane	C_3F_8	76-19-7	188.02	345.05[a]	26.80[a]	299.00[a]	112.03
octafluorotoluene	C_7F_8	434-64-0	236.06	534.47[k]	27.05[k]	428.00[k]	163.15
n-octane	C_8H_{18}	111-65-9	114.23	568.80[b]	24.90[b]	492.00[b]	188.81
1-octene	C_8H_{16}	111-66-0	112.22	566.70[b]	26.20[b]	464.00[b]	177.56
oleic acid	$C_{18}H_{34}O_2$	112-80-1	282.47	781.00[c]	13.90[c]	1000.00[c]	397.05
oleic acid ethyl ester	$C_{20}H_{38}O_2$	111-62-6	310.52	891.97[e]	11.38[e]	1154.20[e]	461.44
oleic acid methyl ester	$C_{19}H_{36}O_2$	112-62-9	296.49	868.65[e]	12.01[e]	1098.65[e]	438.19
oxygen	O_2	7782-44-7	32.00	154.60[b]	50.40[b]	73.40[b]	25.71
palladium(II) acetylacetonate	$C_{10}H_{14}O_4Pd$	14024-61-4	304.64	651.12[d]	4.13[d]	435.41[d]	166.11
palmitic acid ethyl ester	$C_{18}H_{36}O_2$	628-97-7	284.48	835.62[g]	12.36[g]	1061.66[g]	422.74
pentaerythritol	$C_5H_{12}O_4$	115-77-5	136.15	780.00[a]	47.80[a]	381.00[a]	144.43
pentafluorobenzene	C_6HF_5	363-72-4	168.07	530.97[k]	35.31[k]	324.00[k]	121.87
n-pentane	C_5H_{12}	109-66-0	72.15	469.70[b]	33.70[b]	304.00[b]	114.00
2-methyl-2,4-pentanediol	$C_6H_{14}O_2$	107-41-5	118.18	621.00[c]	40.10[c]	398.00[c]	151.19
1-pentanol	$C_5H_{12}O$	71-41-0	88.15	588.20[b]	39.10[b]	326.00[b]	122.66
2-pentanol	$C_5H_{12}O$	6032-29-7	88.15	552.00[a]	38.80[a]	327.00[a]	123.05
3-pentanol	$C_5H_{12}O$	584-02-1	88.15	547.00[a]	38.80[a]	327.00[a]	123.05
2-pentanone	$C_5H_{10}O$	107-87-9	86.13	561.10[b]	36.90[b]	301.00[b]	112.82
3-pentanone	$C_5H_{10}O$	96-22-0	86.13	561.00[b]	37.30[b]	336.00[b]	126.60
2,4-dimethyl-3-pentanone	$C_7H_{14}O$	565-80-0	114.19	576.00[c]	30.20[c]	416.00[c]	158.36
2,2,4,4-tetramethyl-3--pentanone	$C_9H_{18}O$	815-24-7	142.24	627.18[d]	30.29[d]	407.72[d]	155.06
n-pentylbenzene	$C_{11}H_{16}$	538-68-1	148.25	679.90[a]	26.04[a]	550.00[a]	212.20
phenanthrene	$C_{14}H_{10}$	85-01-8	178.23	873.00[b]	29.00[a]	554.00[b]	213.82
phenol	C_6H_6O	108-95-2	94.11	694.20[b]	61.30[b]	229.00[b]	84.71
phenylacetic acid	$C_8H_8O_2$	103-82-2	136.15	783.55[e]	38.50[e]	422.60[e]	161.00
phenylacetylene	C_8H_6	536-74-3	102.14	655.43[a]	44.03[a]	337.50[a]	127.20
phenylbutazone	$C_{19}H_{20}N_2O_2$	50-33-9	308.38	861.18[e]	18.38[e]	933.55[e]	369.44

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M (g·mol^{-1})	T_c (K)	P_c (bar)	V_c (cm^3·mol^{-1})	V_{bp}^{o} (cm^3·mol^{-1})
1-phenyldodecane	$C_{18}H_{30}$	123-01-3	246.44	774.26[a]	15.79[a]	1000.00[a]	397.05
1-phenylethanol	$C_8H_{10}O$	98-85-1	122.17	675.30[f]	40.60[m]	392.15[m]	148.86
2-phenylethanol	$C_8H_{10}O$	60-12-8	122.17	684.00[a]	39.20[a]	387.00[a]	146.81
2-phenylethyl acetate	$C_{10}H_{12}O_2$	103-45-7	164.10	712.23[f]	30.12[f]	524.15[f]	201.76
1-phenylhexane	$C_{12}H_{18}$	1077-16-3	162.28	698.00[a]	23.80[a]	618.00[a]	239.77
phenylmethanol	C_7H_8O	100-51-6	108.14	720.20[b]	44.00[b]	335.00[a]	126.21
1-phenyloctane	$C_{14}H_{22}$	2189-60-8	190.33	729.00[a]	20.20[a]	703.00[a]	274.44
3-phenylpropyl acetate	$C_{11}H_{14}O_2$	122-72-5	178.23	718.70[f]	27.23[f]	580.37[f]	224.50
α-pinene	$C_{10}H_{16}$	80-56-8	136.24	632.00[a]	27.60[a]	504.00[a]	193.64
β-pinene	$C_{10}H_{16}$	127-91-3	136.24	643.00[a]	27.60[a]	506.00[a]	194.44
piperazine	$C_4H_{10}N_2$	110-85-0	86.14	638.00[a]	55.30[a]	310.00[a]	116.36
2-piperidineethanol	$C_7H_{15}NO$	1484-84-0	129.20	745.14[e]	38.73[e]	418.40[e]	159.32
2-phenyl-1-propanol	$C_9H_{12}O$	1123-85-9	136.20	662.02[f]	36.90[f]	443.23[f]	169.24
3-phenyl-1-propanol	$C_9H_{12}O$	122-97-4	136.20	702.30[f]	36.40[f]	455.45[f]	174.14
poly(ethylene glycol) 200	$H(OCH_2CH_2)_nOH$	25322-68-3	~ 200	–	–	–	–
poly(ethylene glycol) 300	$H(OCH_2CH_2)_nOH$	25322-68-3	~ 300	–	–	–	–
poly(ethylene glycol) 400	$H(OCH_2CH_2)_nOH$	25322-68-3	~ 400	–	–	–	–
poly(ethylene glycol) 600	$H(OCH_2CH_2)_nOH$	25322-68-3	~ 600	–	–	–	–
poly(propylene glycol) 400	$H[OCH(CH_3)CH_2]_nOH$	25322-69-4	~ 400	–	–	–	–
potassium chloride	KCl	7447-40-7	74.55	–	–	–	–
propanamide	C_3H_7NO	79-05-0	73.09	718.00[a]	49.80[a]	267.00[a]	99.50
propane	C_3H_8	74-98-6	44.09	369.80[b]	42.50[b]	203.00[b]	74.66
1-propanol	C_3H_8O	71-23-8	60.10	536.80[b]	51.70[b]	219.00[b]	80.84
2,2-pimethyl-1-propanol	$C_5H_{12}O$	75-84-3	88.15	550.00[a]	38.80[a]	327.00[a]	123.05
2-amino-2-methyl-1-propanol	$C_4H_{11}NO$	124-68-5	89.14	619.80[h]	38.62[h]	315.00[h]	118.32
2-propanol	C_3H_8O	67-63-0	60.10	508.30[b]	47.60[b]	220.00[b]	81.23
2-methyl-2-propanol	$C_4H_{10}O$	75-65-0	74.12	506.20[a]	39.72[a]	275.00[a]	102.63
propene	C_3H_6	115-07-1	42.08	364.90[b]	46.00[b]	181.00[b]	66.21
i-propylbenzene	C_9H_{12}	98-82-8	120.20	631.10[b]	32.10[b]	427.70[a]	163.03
n-propylbenzene	C_9H_{12}	103-65-1	120.20	638.20[b]	32.00[b]	440.00[b]	167.95
propylene glycol	$C_3H_8O_2$	57-55-6	76.09	626.00[a]	61.00[a]	239.00[a]	88.59
pyrene	$C_{16}H_{10}$	129-00-0	202.26	936.00[a]	26.10[a]	630.00[a]	244.65
radon	Rn	10043-92-2	222.00	377.40[a]	63.00[a]	140.00[a]	50.58
rubidium chloride	RbCl	7791-11-9	120.92	–	–	–	–
salicylic acid	$C_7H_6O_3$	69-72-7	138.12	739.00[a]	51.80[a]	364.00[a]	137.68
serine	$C_3H_7NO_3$	302-84-1	105.09	804.97[e]	61.20[e]	268.35[e]	100.03

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M ($g \cdot mol^{-1}$)	T_c (K)	P_c (bar)	V_c ($cm^3 \cdot mol^{-1}$)	V_{bp}^{o} ($cm^3 \cdot mol^{-1}$)
sodium chloride	$NaCl$	7647-14-5	58.44	–	–	–	–
strontium chloride	$SrCl_2$	10476-85-4	158.53	–	–	–	–
squalene	$C_{30}H_{50}$	111-02-4	410.72	974.94[d]	13.23[d]	1128.14[d]	450.53
stearic acid	$C_{18}H_{36}O_2$	57-11-4	284.48	803.00[h]	13.30[h]	1140.00[h]	455.49
stearic acid ethyl ester	$C_{20}H_{40}O_2$	111-61-5	312.54	777.90[h]	10.19[h]	1380.00[h]	556.47
styrene	C_8H_8	100-42-5	104.15	647.00[b]	39.90[a]	352.00[a]	132.93
sucrose	$C_{12}H_{22}O_{11}$	57-50-1	342.30	1086.00[c]	26.90[c]	761.00[c]	298.22
sulfolane	$C_4H_8O_2S$	126-33-0	120.17	849.00[a]	50.30[a]	300.00[a]	112.43
sulfur dioxide	SO_2	7446-09-5	64.06	430.75[a]	78.84[a]	122.00[a]	43.79
sulfur hexafluoride	SF_6	2551-62-4	146.05	318.70[b]	37.60[b]	198.80[b]	73.04
tetrabutyltin	$C_{16}H_{36}Sn$	1461-25-2	347.17	767.97[d]	17.25[d]	760.75[d]	298.12
tetrachloroethene	C_2Cl_4	127-18-4	165.83	620.20[b]	47.60[b]	289.60[b]	108.35
n-tetradecane	$C_{14}H_{30}$	629-59-4	198.39	693.00[b]	14.40[b]	830.00[b]	326.62
1-tetradecene	$C_{14}H_{28}$	1120-36-1	196.38	691.00[h]	16.27[h]	865.00[h]	341.07
tetraethylene glycol	$C_8H_{18}O_5$	112-60-7	194.23	722.00[a]	25.90[a]	564.00[a]	217.86
tetraethyltin	$C_8H_{20}Sn$	597-64-8	234.95	655.92[d]	25.75[d]	429.28[d]	163.66
1,2,3,5-tetrafluorobenzene	$C_6H_2F_4$	2367-82-0	150.08	555.49[e]	36.40[e]	351.05[e]	132.55
1,2,4,5-tetrafluorobenzene	$C_6H_2F_4$	327-54-8	150.08	535.25[k]	37.47[k]	351.05[e]	132.55
tetrafluoromethane	CF_4	75-73-0	88.01	227.60[b]	37.40[b]	139.60[b]	50.43
tetrahydrofuran	C_4H_8O	109-99-9	72.11	540.10[b]	51.90[b]	224.00[b]	82.78
tetramethyltin	$C_4H_{12}Sn$	594-27-4	178.85	511.77[d]	34.18[d]	263.54[d]	98.15
tetrapropyltin	$C_{12}H_{28}Sn$	2176-98-9	291.06	759.88[d]	20.66[d]	595.01[d]	230.44
thenoyltrifluoroacetone	$C_8H_5F_3O_2S$	326-91-0	222.18	838.69[d]	26.32[d]	428.15[d]	163.21
threonine	$C_4H_9NO_3$	80-68-2	119.12	859.80[e]	60.67[e]	304.40[e]	114.15
α-tocopherol	$C_{29}H_{50}O_2$	59-02-9	430.71	964.30[l]	10.80[l]	1720.00[l]	700.94
toluene	C_7H_8	108-88-3	92.14	591.80[b]	41.00[b]	316.00[b]	118.72
triarachidonin	$C_{63}H_{98}O_6$	23314-57-0	951.45	1499.66[d]	6.51[d]	2341.53[d]	968.46
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	120-82-1	181.45	725.00[a]	37.20[a]	395.00[a]	150.00
1,1,1-trichloroethane	$C_2H_3Cl_3$	71-55-6	133.41	545.00[b]	43.00[b]	281.00[a]	104.98
trichloromethane	$CHCl_3$	67-66-3	119.37	536.40[a]	54.72[a]	239.00[a]	88.59
trierucin	$C_{69}H_{128}O_6$	2752-99-0	1053.75	1549.28[d]	5.62[d]	2832.93[d]	1182.46
1,2,4-trifluorobenzene	$C_6H_3F_3$	367-23-7	132.09	558.22[e]	38.98[e]	335.05[e]	126.23
triethanolamine	$C_6H_{15}NO_3$	102-71-6	149.19	772.10[c]	27.43[c]	472.00[c]	180.77
triethylene glycol	$C_6H_{14}O_4$	112-27-6	150.18	700.00[a]	33.20[a]	443.00[a]	169.15
trifluoroacetylacetone	$C_5H_5F_3O_2$	367-57-7	154.09	594.02[g]	32.89[g]	365.58[g]	138.31
1,3,5-trimethylbenzene	C_9H_{12}	108-67-8	120.20	637.30[b]	31.30[b]	433.00[a]	165.15

Table 3.2 (*Continued*)

Substance	Formula	CAS Number	M $(g \cdot mol^{-1})$	T_c (K)	P_c (bar)	V_c $(cm^3 \cdot mol^{-1})$	V_{bp} [o] $(cm^3 \cdot mol^{-1})$
2,2,4-trimethylpentane	C_8H_{18}	540-84-1	144.23	543.80[a]	25.70[a]	468.00[a]	179.17
trinervonin	$C_{75}H_{140}O_6$	81913-24-8	1137.91	1601.10[d]	5.20[d]	3081.54[d]	1291.44
triolein	$C_{57}H_{104}O_6$	122-32-7	885.43	1640.00[c]	4.70[c]	3090.00[c]	1295.15
s-trioxane	$C_3H_6O_3$	110-88-3	90.08	604.00[a]	58.20[a]	206.00[a]	75.82
ubiquinone CoQ10	$C_{59}H_{90}O_4$	303-98-0	863.34	1522.50[d]	7.09[d]	2146.17[d]	883.95
n-undecane	$C_{11}H_{24}$	1120-21-4	156.31	638.80[b]	19.70[b]	660.00[b]	256.88
6-undecanone	$C_{11}H_{22}O$	927-49-1	170.30	678.01[c]	20.46[c]	657.50[c]	255.86
valine	$C_5H_{11}NO_2$	516-06-3	117.15	741.96[e]	42.39[e]	356.50[e]	134.71
vanillin	$C_8H_8O_3$	121-33-5	152.15	777.00[a]	40.10[a]	415.00[a]	157.96
vitamin K_1	$C_{31}H_{46}O_2$	84-80-0	452.71	1329.54[e]	8.58[e]	1620.20[e]	658.37
vitamin K_3	$C_{11}H_8O_2$	58-27-5	172.18	893.85[e]	31.96[e]	537.20[e]	207.03
water	H_2O	7732-18-5	18.02	647.30[b]	221.20[b]	57.10[b]	19.76
xenon	Xe	7440-63-3	131.30	289.70[b]	58.40[b]	118.40[b]	42.43
m-xylene	C_8H_{10}	108-38-3	106.17	617.10[b]	35.40[b]	376.00[b]	142.44
5-*tert*-butyl-*m*-xylene	$C_{12}H_{18}$	98-19-1	162.28	684.85[f]	23.90[f]	591.75[f]	229.11
p-xylene	C_8H_{10}	106-42-3	106.17	616.20[b]	35.10[b]	379.00[b]	143.63
o-xylene	C_8H_{10}	95-47-6	106.17	630.30[b]	37.30[b]	369.00[b]	139.67
xylitol	$C_5H_{12}O_5$	87-99-0	152.15	1032.99[h]	63.20[h]	399.00[h]	151.59
xylose	$C_5H_{10}O_5$	58-86-6	150.13	953.50[h]	65.88[h]	388.00[h]	147.21
[Bmim][BF_4]	$C_8H_{15}N_2BF_4$	174501-65-6	226.02	643.20[n]	20.40[n]	655.00[n]	254.84
[Bmim][bti]	$C_{10}H_{15}N_3F_6S_2O_4$	174899-83-3	419.40	1269.90[n]	27.60[n]	990.10[n]	392.93
[Bmim][CF_3SO_3]	$C_9H_{15}N_2F_3SO_3$	174899-66-2	288.30	1023.50[n]	29.50[n]	750.70[n]	293.99
[Bmim][Cl]	$C_8H_{15}N_2Cl$	79917-90-1	174.67	789.00[n]	27.80[n]	568.80[n]	219.81
[Bmim][$MeSO_4$]	$C_9H_{18}N_2SO_4$	401788-98-5	250.32	1081.60[n]	36.10[n]	716.90[n]	280.13
[Bmim][$OcSO_4$]	$C_{16}H_{32}N_2SO_4$	445473-58-5	348.50	1189.80[n]	20.20[n]	1116.70[n]	445.74
[Bmim][PF_6]	$C_8H_{15}N_2PF_6$	174501-64-5	284.18	719.40[n]	17.30[n]	762.50[n]	298.84
[Emim][BF_4]	$C_6H_{11}N_2BF_4$	143314-16-3	197.97	596.20[n]	23.60[n]	540.80[n]	208.48
[Emim][bti]	$C_8H_{11}N_3F_6S_2O_4$	174899-82-2	391.31	1249.30[n]	32.70[n]	875.90[n]	345.57
[Emim][$C_2H_5SO_4$]	$C_8H_{16}N_2SO_4$	342573-75-5	236.30	1067.50[n]	40.50[n]	659.80[n]	256.80
[Emim][C_2N_3]	$C_8H_{11}N_5$	370865-89-7	177.20	999.00[n]	29.10[n]	597.80[n]	231.57
[Emim][CF_3SO_3]	$C_9H_{15}N_2F_3SO_3$	174899-66-2	288.29	992.30[n]	35.80[n]	636.40[n]	247.26
[Emim][$MDEGSO_4$]	$C_{11}H_{22}N_2SO_6$	790663-77-3	310.40	1162.90[n]	28.10[n]	862.30[n]	339.95
[Hmim][bti]	$C_{12}H_{19}N_3F_6S_2O_4$	382150-50-7	447.42	1292.80[n]	23.90[n]	1104.40[n]	440.60
[Omim][bti]	$C_{14}H_{23}N_3F_6S_2O_4$	178631-04-4	475.50	1317.80[n]	21.00[n]	1218.60[n]	488.46

[a] Taken from Yaws, 1998 [3]; [b] Taken from Reid *et al.* [10]; [c] Taken from Yaws, 2008 [14]; [d] Estimated by the Klincewicz [10, 21] method; [e] Average of the values by the Joback [10, 17-18] and Ambrose [10, 19-20] methods; [f] Average of the values by the Joback [10, 17-18] and Wen-Qiang [23] methods; [g] Average of the values by the Joback [10, 17-18] and Somayajulu [22] methods; [h] Taken from DIPPR database [2]; [i] Taken from Table 4 of Liu and Ruckenstein [15]; [j] Average of the values by the Joback [10, 17-18] and Constantinou-Gani [24] methods; [k] Taken from Korea Thermophysical Properties Data Bank (KDB) [16]; [l] Taken from ASPEN database [271]; [m] Estimated by the Joback [10, 17-18] method; [n] Taken from Valderrama and Rojas [25]; [o] Estimated by Tyn-Calus [10, 26] expression; Note: An hyphen means that data is not available.

Nomenclature

M	Molecular weight, $\mathrm{g \cdot mol^{-1}}$
NDP	Number of data points
P_c	Critical pressure, bar
$P_{\mathrm{r},1}$	Reduced pressure of the solvent using critical pressure
T_c	Critical temperature, K
$T_{\mathrm{r},1}$	Reduced temperature of the solvent using critical temperature
V_bp	Molar volume at normal boiling point, $\mathrm{cm^3 \cdot mol^{-1}}$
V_c	Critical volume, $\mathrm{cm^3 \cdot mol^{-1}}$

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4. New Models and Modelling Results

This chapter focus all modelling results obtained in this work. The new expressions derived for binary diffusion coefficients at infinite dilution of model and real systems are presented and validated with the database compiled in Chapter 3. The calculated results are compared with other equations taken from literature. The models derived by Liu, Silva and Macedo (TLSM and $\mathrm{TLSM_d}$) [1] were also revisited in order to test their applicability with our new and large database.

4.1. Revisiting Liu-Silva-Macedo Expressions

Taking into account the theoretically sound development of the models of Liu, Silva and Macedo [1] their predictive (TLSM, Eq. (2.64)) and 1-parameter ($\mathrm{TLSM_d}$, Eqs. (2.64) + + (2.81) and (2.82)) equations were revisited in this work with the objective to test them with a much larger database: 296 systems/4256 experimental diffusivities against the original 77 systems/1033 data points. This has been the subject of Paper I presented in the following. As mentioned in the Chapter 2, the global errors reported by the original authors in 1997 were 14.77% and 6.57%, for TLSM and $\mathrm{TLSM_d}$, respectively. Their application to the whole database provided $\mathrm{AARD}(\mathrm{TLSM}) = 15.71\%$ and $\mathrm{AARD}(\mathrm{TLSM_d}) = 3.89\,\%$ for gaseous, liquid, and supercritical systems. Nonetheless it must be emphasized that they should be only used for non-polar or weakly polar solvents.

4.2. New Models Developed

Most models found in literature usually fail when applied over wide ranges of temperature and density values, and in systems involving polar molecules and/or very asymmetric components (in terms of mass and size). In order to address these limitations, this work targeted the development of accurate D_{12} models validated using our large database. A brief description of these models is provided in the following.

An accurate HS model was developed (Paper II), establishing an explicit dependence of F_{12} on the reduced number density of the solvent, and on masses and diameters ratios of solute and solvent. It provides a very good representation of 43 MD data from Herman and Alder [2] and Alder *et al.* [3] (AARD = 4.44%). Simultaneously, a molecularly based model for real systems was devised according to the Rice and Gray approach (Paper II) and embodying the new HS expression, where the softness of the repulsive interactions were taken into account *via* the effective hard sphere diameter method. It involves one parameter and achieves an AARD = 4.26% for 309 systems containing 5341 data points, and interpret equally well the diffusion phenomena in gases, liquid and supercritical fluids. A distinct expression (Paper III) was derived once again using the new HS equation, but in this case the contribution of attractive forces was considered by coupling an attractive exponential term. With just one parameter, it provides a global AARD = 4.40% for 319 binary systems and 5421 data points including gas, liquid and supercritical fluids.

Attending to the nature of the databases used to validate the two previous equations, they may be only applied to non-polar or weakly polar binaries. Hence a more general model (Paper IV) was later developed for the diffusivities of systems containing at least one polar component (solute and/or solvent). This is a sensitive case for which the existing equations in literature usually fail, particularly when hydrogen-bonding solvents are involved. The new model includes friction coefficients in the Rice and Gray seminal equation to reflect a repulsive hard sphere core, a soft LJ contribution, and a specific polar interaction. With two parameters, it provides an error of 3.65% for 211 polar systems and 3463 data points, and 4.27% for systems with strictly polar solvents (141 systems/1994 experimental points).

A new hybrid free-volume equation (Paper V) was presented for supercritical carbon dioxide and liquid water due to the large importance of both solvents in research and industry. There, the repulsive and attractive interactions were contemplated by the concepts of free volume and activation energy, respectively. This model embodies one parameter that is system specific, and achieves an $\text{AARD} = 3.56\%$ for 289 systems and 5485 data points.

More recently, an universal equation (Paper VI) based on the LJ model applicable to gas, liquid and supercritical states was published for accurate calculation of tracer diffusivities for polar, weakly polar, and non-polar solutes and/or solvents. It requires two parameters, namely the molecular diameter of the solvent and a diffusion activation energy and reaches $\text{AARD} = 2.65\%$ for polar (180 systems/2335 points) and $\text{AARD} = 2.97\%$ for non-polar or weakly polar (307 systems/5958 points) mixtures, totalizing 487 systems with 8293 points.

In the whole, the good results attained by the previous models result from their solid physical principles. Furthermore, all of them exhibit an excellent extrapolation ability. Some spreadsheets for the calculation of diffusivities are provided online as supplementary material of the original papers to help readers in calculations.

Empirical and semi-empirical models (Paper VII) dependent only on temperature and/or solvent density and/or solvent viscosity were published afterwards, where the main objective was to provide very simple and accurate equations for D_{12}. They involve two system specific parameters and reach global AARDs between 2.78% (when D_{12} is correlated with temperature and solvent viscosity) and 4.44% (for D_{12} when it only depends upon solvent viscosity) for 539 binary systems and 8219 data points in liquid and supercritical fluids. These equations exhibit also very good extrapolation ability.

Since previous models require at least one parameter that must be obtained a priori by fitting experimental diffusivities, it is fundamental to have accurate expressions for their pure prediction. In this respect, hydrodynamic equations are good alternatives, since they are simple, involve a small set of input data, and are frequently predictive. However, with the expressions available in literature (see Table 2.2) significant errors are frequently found, particularly when they are applied over large ranges of temperature and density, or near the critical point. Hence, two modified Stokes-Einstein equations (Paper VIII) were proposed for the pure prediction of D_{12} values of solutes in supercritical carbon dioxide. The validation involved once again our large database, comprehending extremely distinct molecules in terms of size, molecular weight, polarity and sphericity (156 systems totalizing 4425 data points). The global deviations found for both models are inferior to

6.80%, while well-known hydrodynamic expressions like Wilke-Chang [4-6], Tyn--Calus [5, 7], Scheibel [6, 8], Lusis-Ratcliff [6, 9], Reddy-Doraiwasmy [6, 10], and Lai Tan [11] provide errors between 12.17% and 79.34%.

In Table 4.1 the aforementioned models developed in this work for tracer diffusion coefficients of real systems are summarized. Each row is devoted to a specific paper and gives information about fundamentals, input data for the calculations, number and identification of specific system parameter(s), the physical states tested, the type of compounds, the number of systems (NS), number of data points (NDP), and global average absolute relative deviations (AARD).

Table 4.1. Expressions for D_{12} of real system developed and/or validated in this work (fundamentals, input data, parameters, physical state, type of compounds, number of systems (NS), number of data points (NDP), and global average absolute relative deviation (AARD)).

Paper	Model fundamentals	Input data	Number of parameters	Physical state	Compounds	NS	NDP	AARD (%)
I	Lennard-Jones (LJ) model	T, ρ_1, M_1, M_2, $T_{c,1}$, $T_{c,2}$, $P_{c,1}$, $P_{c,2}$, $V_{c,2}$	0 or 1 ($k_{12,d}$)	L, G and SCF	Solvents: non-polar or weakly polar; Solutes: All type	296	5279	15.71 or 3.89
II	Rice and Gray approach	T, ρ_1, M_1, M_2, $T_{c,1}$, $T_{c,2}$, $V_{c,1}$, $V_{c,2}$	1 ($k_{12,d}$)	L, G and SCF	Solvents: non-polar or weakly polar; Solutes: All type	309	5341	4.26
III	Exponential activation term to represent attractive forces	T, ρ_1, M_1, M_2, $T_{c,1}$, $T_{c,2}$, $P_{c,1}$, $P_{c,2}$	1 (E_D)	L, G and SCF	Solvents: non-polar or weakly polar; Solutes: All type	314	5421	4.40
IV	Rice and Gray approach and Stockmayer potential	T, ρ_1, M_1, M_2, μ_1, μ_2, $T_{bp,1}$, $V_{bp,1}$, $T_{c,1}$, $T_{c,2}$, $V_{c,1}$, $V_{c,2}$	2 (k_{12}, A_{12})	L, G and SCF	Systems containing at least one polar component (solute and/or solvent)	211	3463	3.65
V	Concepts of free volume and activation energy	T, ρ_1, M_2	1 (E_a)	L and SCF	Solvents: Supercritical CO_2 and liquid water; Solutes: All type	289	5485	3.56
VI	LJ model with an exponential activation term	T, ρ_1, M_1, M_2, $T_{c,1}$, $T_{c,2}$, $P_{c,1}$, $P_{c,2}$, $V_{c,2}$	2 ($\sigma_{1,LJ}$, E_D)	L, G and SCF	All type of solvents and solutes	487	8293	2.74
VII	Empirical and semi-empirical relations	T, ρ_1, η_1	2 (a_i, b_i)	L and SCF	All type of solvents and solutes	539	8219	2.78 – 4.44
VIII	Modified Stokes-Einstein equations	T, η_1, M_2, $V_{bp,2}$, $T_{bp,2}$, $T_{c,2}$, $P_{c,2}$	–	SCF	Solvent: Supercritical CO_2; Solutes: All type of solutes	156	4425	6.38 and 6.75

L – Liquid; G – Gas; SCF – Supercritical

Nomenclature

AARD	Average absolute relative deviation
M	Molecular weight
NDP	Number of data points
NS	Numbrer of systems
P_c	Critical pressure, bar
T_{bp}	Normal boiling point
T_c	Critical temperature
V_{bp}	Molar volume at normal boiling point
V_c	Critical volume

Greek letters

η_1	Solvent viscosity
μ	Dipole moment
ρ_1	Solvent density

Subscripts

1	Solvent
2	Solute

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Paper I

Adapted from

Revisiting the Liu-Silva-Macedo Model for Tracer Diffusion Coefficients of Supercritical, Liquid, and Gaseous Systems

Industrial & Engineering Chemistry Research, **2010**, 49, 7697–7700.

Abstract

This work comprises two main purposes: to present the largest database of tracer diffusion coefficients ever published, comprehending 5279 experimental points and 296 binary systems, and provide the necessary Lennard-Jones diameter and energy, and interaction parameter of the Liu-Silva-Macedo correlation ($\mathrm{TLSM_d}$), since it affords reliable and very good results for all systems studied (the global deviation found was 3.89%). For comparison, the well-known equations of Dymond-Hildebrand-Batschinsky, Zhu and co-workers, and Tyn-Calus have been adopted.

4.PI.1. Introduction

The tracer diffusion coefficients, D_{12}, are fundamental properties for the design of heterogeneous chemical reactors and rate-controlled separation processes. Its importance is essential for concentrated solutions also, whether binary or multicomponent, where Maxwell-Stefan (MS) approach is highly recommended. In fact, the necessary crossed MS diffusivities may be estimated from the binary ones at infinite dilution taking into account relations of the Vignes type [1].

With respect to modelling, most of the existing expressions to correlate or predict D_{12} are based on hydrodynamic theory, kinetic theory, absolute-rate theory of Eyring, free volume theory, and models devised for simple idealized fluids such as hard-sphere, square-well, Weeks-Chandler-Andersen, and Lennard-Jones. A detailed description of these approaches may be found elsewhere [2-4].

Since 1990 several models for D_{12} have been published. A very recent paper by Suárez-Iglesias *et al.* [5] pointed out that «the models of Ruckenstein and Liu [6], Liu *et al.* [7] and Dariva *et al.* [8-9] can be considered the most significant proposed between 1990-2000 because of their general validity (applicable over wide ranges of temperature and pressure for non-hydrogen-bonding compounds) and the possibility of using them to estimate binary diffusion coefficients of solutes at infinite dilution». In particular, the predictive equation by Liu, Silva and Macedo, hereafter denoted by TLSM, published in 1997 in this journal [10], presented an absolute average relative deviation AARD = 14.77% for 1033 data points and 77 binary systems, while a derived one-parameter correlation, henceforth labelled $\mathrm{TLSM_d}$, accomplished AARD = 6.57% for the same database. The good results achieved by TLSM$_d$ expression induced us to revisit both models in order to facilitate and expand their application by reporting the implied parameters.

Accordingly, this Research Note comprises two main purposes: to make available the largest database of tracer diffusivities ever compiled up till now (5279 experimental points from 296 binary systems), and present the TLSM$_d$ LJ constants and interaction parameter for all systems analysed. Results are compared with those from the three well known equations of Dymond-Hildebrand-Batschinsky [3-4, 11], Zhu *et al.* [12], and Tyn-Calus [2, 13].

4.PI.2. TLSM Predictive Model (Zero Parameters)

The tracer diffusion coefficient model due to Liu, Silva and Macedo [10], TLSM, corresponds to the following set of equations:

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{21.16}{\rho_1\,\sigma_{12,\mathrm{eff}}^2}\left(\frac{1000\Re_\mathrm{g}\,T}{2M_{12}}\right)^{\frac{1}{2}}\exp\left(-\frac{0.75\rho_1^*}{1.2588-\rho_1^*}-\frac{0.27862}{T_{12}^*}\right) \qquad (1)$$

where subscripts 1 and 2 stand for solvent and solute, respectively, $\Re_\mathrm{g}=8.3144\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ is the universal gas constant, ρ_1 (cm^{-3}) is solvent number density, and T is absolute temperature; the reduced number density of solvent (ρ_1^*), reduced temperature (T_{12}^*), and reduced molar mass of the system (M_{12}, $\mathrm{g\cdot mol^{-1}}$) are calculated by:

$$\rho_1^*=\rho_1\sigma_{1,\mathrm{eff}}^3 \qquad (2)$$

$$T_{12}^*=\frac{T}{\varepsilon_{12,\mathrm{LJ}}/k_\mathrm{B}} \qquad (3)$$

$$M_{12}=\frac{M_1M_2}{M_1+M_2} \qquad (4)$$

where k_B is the Boltzmann constant, and $\sigma_{12,\mathrm{LJ}}$ and $\varepsilon_{12,\mathrm{LJ}}$ are the binary LJ parameters (diameter and energy) computed from the single ones by the following combining rules:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \frac{\sqrt{\sigma_{1,\mathrm{LJ}}^3\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right)\times\sigma_{2,\mathrm{LJ}}^3\left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)}}{\sigma_{12,\mathrm{LJ}}^3} \tag{5}$$

$$\sigma_{12,\mathrm{LJ}} = \frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \tag{6}$$

The effective binary and single diameters, $\sigma_{12,\mathrm{eff}}$ and $\sigma_{1,\mathrm{eff}}$, take into account the influence of temperature upon the LJ diameters. An equation of the Boltzmann type has been adopted for their calculation [7, 10, 14]:

$$\sigma_{n,\mathrm{eff}} = \sigma_{n,\mathrm{LJ}}2^{1/6}\left[1+\sqrt{1.3229T_n^*}\right]^{-1/6} \tag{7}$$

where subscript n equals 1 or 12, and $T_n^* = T/(\varepsilon_{n,\mathrm{LJ}}/k_\mathrm{B})$. The LJ force constants may be taken from the original article [7] or, for substances not covered in that essay, are calculated by the corresponding states correlations (with critical constants in K and bar) [14]:

$$\frac{\varepsilon_\mathrm{LJ}}{k_\mathrm{B}}(\mathrm{K}) = 0.774T_\mathrm{c} \tag{8}$$

$$\sigma_\mathrm{LJ}^3\left(\mathrm{Å}^3\right) = 0.17791+11.779\left(\frac{T_\mathrm{c}}{P_\mathrm{c}}\right)-0.049029\left(\frac{T_\mathrm{c}}{P_\mathrm{c}}\right)^2 \tag{9}$$

Eq. (9) may be adopted successfully for $T_\mathrm{c}/P_\mathrm{c} < 100$. For higher values, one may estimate LJ diameter by a relation provided by the principle of corresponding states [2, 15-16] $\sigma_\mathrm{LJ}(\mathrm{Å}) = 0.809\,V_\mathrm{c}^{1/3}$, where V_c is critical volume in $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$. By doing so the TLSM and TLSM$_\mathrm{d}$ equations may be extended to higher molecular weight solutes.

Summarily, the prediction of D_{12} at temperature T and solvent number density ρ_1 may be accomplished by knowing only three input parameters per molecule: molecular weight, and LJ diameter and energy. All data are tabled in this Research Note for the 296 binary systems studied.

4.PI.3. TLSM$_\mathrm{d}$ Correlation Model (One Parameter)

From TLSM model it is possible to generate a one–parameter correlation by inserting the interaction constant $k_{12,\mathrm{d}}$ only into the diameter combining rule (Eq. (6)). Accordingly, Eqs. (5) and (6) become:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \frac{8\sqrt{\sigma_{1,\mathrm{LJ}}^3(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B})\times\sigma_{2,\mathrm{LJ}}^3(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B})}}{(\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}})^3} \tag{10}$$

$$\sigma_{12,\mathrm{LJ}} = (1-k_{12,\mathrm{d}})\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \tag{11}$$

Summarily, D_{12} can be predicted by TLSM$_\mathrm{d}$ model as function of T and ρ_1 by knowing just three input parameters per molecule (M, σ_LJ and $\varepsilon_\mathrm{LJ}/\mathrm{k_B}$) and the binary interaction constant $k_{12,\mathrm{d}}$. Once more, all values of interest are tabled in this Research Note for the 296 binary systems studied.

4.PI.4. Data Sources and Data for Pure Substances

To carry out a strict validation of both TLSM and TLSM$_\mathrm{d}$ models and extend their application to much more systems than those presented in the original paper [10], the largest database ever used has been compiled. It comprehends globally 296 binary systems performing 5279 experimental diffusivities: 168 supercritical systems with 4256 points, 91 liquid systems with 601 points, and 37 gaseous systems with 422 points. Table 3.1 (Chapter 3) contains the systems studied in this work, along with the data sources, number of data points (NDP), and reduced ranges of temperature, pressure and density for each system (here the reduction is accomplished with critical constants). The data for pure substances necessary for the calculations are presented in Table 3.2 (Chapter 3).

4.PI.5. Calculation Results

In Table 1 the individual results achieved with TLSM and TLSM$_\mathrm{d}$ models are also compiled, namely the AARDs and the interaction binary parameters $k_{12,\mathrm{d}}$. Some few authors do not report the solvent densities of their data. In these cases they have been calculated by the correlations of Pitzer and Schreiber [17] for CO_2, and Hankinson-

-Brobst-Thomson [2, 18] for other fluids. Concerning the non-reported viscosities, which are necessary for the Tyn- Calus equation adopted for comparison in this work, they have been estimated by the correlations of Mehrotra [19], for liquid hydrocarbons, and Altunin and Sakhabetdinov [20], for carbon dioxide.

Table 1. Calculated results.

System			TLSM	TLSM_d	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,\text{d}}$	AARD
	Supercritical Systems				
carbon dioxide	acetone	178	7.92	0.03450	4.15
carbon dioxide	acridine	6	16.10	0.07836	1.95
carbon dioxide	allylbenzene	15	11.65	0.06975	2.99
carbon dioxide	aniline	15	7.77	-0.03356	2.98
carbon dioxide	anisole	15	8.94	0.04685	2.06
carbon dioxide	anthracene	22	27.81	0.14875	3.88
carbon dioxide	arachidonic acid (AA)	75	21.43	0.11672	2.13
carbon dioxide	AA ethyl ester	48	24.51	0.13294	2.43
carbon dioxide	behenic acid ethyl ester	17	26.95	0.14261	3.66
carbon dioxide	benzene	222	14.69	0.08974	7.45
carbon dioxide	benzoic acid	29	16.99	0.09276	5.70
carbon dioxide	benzyl acetate	15	10.03	0.05359	2.21
carbon dioxide	benzylacetone	15	8.55	0.04500	2.32
carbon dioxide	biphenyl	24	19.61	0.10845	3.41
carbon dioxide	2-bromoanisole	15	10.73	0.05829	2.37
carbon dioxide	bromobenzene	15	13.06	0.06305	4.63
carbon dioxide	2-butanone	38	16.77	0.08829	1.91
carbon dioxide	*n*-butylbenzene	15	14.55	0.07994	1.90
carbon dioxide	*tert*-butylbenzene	15	15.15	0.09036	3.87
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	15.29	0.08383	2.20
carbon dioxide	butyric acid ethyl ester	16	17.21	0.08676	3.64
carbon dioxide	caffeine	21	9.73	0.03340	8.05
carbon dioxide	capric acid ethyl ester	16	22.35	0.11632	3.85
carbon dioxide	caprylic acid ethyl ester	16	19.72	0.10496	2.93
carbon dioxide	β-carotene	90	20.78	0.10901	1.38
carbon dioxide	chlorobenzene	15	8.63	0.04347	3.92
carbon dioxide	chrysene	4	31.87	0.16983	1.45
carbon dioxide	citral	15	20.87	0.10759	3.19

Table 1 (*Continued*)

System			TLSM	TLSM_d	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,\text{d}}$	AARD
carbon dioxide	cobalt(III) acetylacetonate	38	1.88	0.00682	1.59
carbon dioxide	copper(II) trifluoroacetylacetonate	12	17.80	-0.08244	4.73
carbon dioxide	15-crown-5	29	25.45	0.14571	5.18
carbon dioxide	cycloheptanone	8	14.57	0.06632	2.95
carbon dioxide	cyclononanone	8	14.98	0.07448	3.25
carbon dioxide	cyclopentanone	8	3.91	0.01800	1.04
carbon dioxide	*n*-decane	5	41.43	0.22524	3.70
carbon dioxide	dibenzo-24-crown-8	28	25.90	0.14589	2.06
carbon dioxide	dibenzyl ether	15	9.55	0.05144	2.14
carbon dioxide	1,2-dichlorobenzene	15	16.63	0.08502	1.48
carbon dioxide	*p*-dichlorobenzene	13	14.25	0.06711	3.54
carbon dioxide	diethyl ether	15	16.97	-0.02103	16.55
carbon dioxide	1,2-diethylbenzene	15	14.41	0.07677	1.79
carbon dioxide	1,4-diethylbenzene	15	14.13	0.07720	2.98
carbon dioxide	diisopropyl ether	15	14.79	0.03391	12.60
carbon dioxide	2,4-dimethyl-3-pentanone	8	3.25	-0.00017	3.25
carbon dioxide	2,3-dimethylaniline	15	4.01	0.01766	1.95
carbon dioxide	2,6-dimethylaniline	15	4.62	0.02213	2.66
carbon dioxide	1,1'-dimethylferrocene	68	7.83	0.04437	2.78
carbon dioxide	2,3-dimethylnaphthalene	3	19.16	0.10047	1.29
carbon dioxide	2,6-dimethylnaphthalene	6	17.57	0.09742	3.84
carbon dioxide	2,7-dimethylnaphthalene	6	20.15	0.09184	4.35
carbon dioxide	2,4-dimethylphenol	15	5.14	0.02223	2.58
carbon dioxide	diolein	9	23.52	0.12451	1.64
carbon dioxide	1,3-divinylbenzene	15	17.24	0.08850	1.09
carbon dioxide	docosahexaenoic acid (DHA)	63	19.56	0.10524	1.38
carbon dioxide	DHA ethyl ester	65	25.81	0.13878	2.28
carbon dioxide	DHA methyl ester	17	26.15	0.13998	2.99
carbon dioxide	*n*-dodecane	5	47.19	0.25928	5.39
carbon dioxide	eicosapentaenoic acid (EPA)	55	21.19	0.11480	1.20
carbon dioxide	EPA ethyl ester	48	25.01	0.13391	2.80
carbon dioxide	EPA methyl ester	17	22.87	0.12124	3.62
carbon dioxide	ethanol	24	32.30	0.18276	3.00
carbon dioxide	ethyl acetate	15	19.65	0.01721	19.64
carbon dioxide	ethyl benzoate	15	16.97	0.07820	4.93

Table 1 (*Continued*)

System			TLSM	TLSM$_d$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,d}$	AARD
carbon dioxide	ethylbenzene	15	17.48	0.09142	2.07
carbon dioxide	2-ethyltoluene	15	13.96	0.07787	3.28
carbon dioxide	3-ethyltoluene	15	14.42	0.07505	3.59
carbon dioxide	4-ethyltoluene	15	11.85	0.06181	2.68
carbon dioxide	eugenol	15	4.75	0.02183	3.36
carbon dioxide	ferrocene	98	27.74	0.15664	3.88
carbon dioxide	2-fluoroanisole	15	7.58	0.04081	1.66
carbon dioxide	fluorobenzene	15	5.58	0.02651	3.64
carbon dioxide	*n*-heptane	5	33.05	0.17552	3.31
carbon dioxide	2-heptanone	11	37.88	0.20301	4.47
carbon dioxide	4-heptanone	9	44.44	0.25169	2.19
carbon dioxide	hexachlorobenzene	14	25.93	0.15688	7.77
carbon dioxide	1,1,1,5,5,5-hexafluoroacetylacetone	15	6.66	0.03641	4.08
carbon dioxide	*n*-hexane	5	29.45	0.14894	2.85
carbon dioxide	iodobenzene	15	10.31	0.05395	3.28
carbon dioxide	D-limonene	15	19.74	0.10763	3.15
carbon dioxide	linalool	15	16.58	0.08350	3.49
carbon dioxide	linoleic acid	71	12.78	0.07315	3.25
carbon dioxide	α-linolenic acid	56	14.48	0.07553	1.83
carbon dioxide	γ-linolenic acid	142	21.27	0.11542	2.79
carbon dioxide	γ-linolenic acid ethyl ester	41	16.79	0.09357	6.27
carbon dioxide	linoleic acid methyl ester	21	21.04	0.10940	1.40
carbon dioxide	γ-linolenic acid methyl ester	52	21.01	0.11043	5.39
carbon dioxide	methanol	10	14.40	0.08572	3.90
carbon dioxide	2-methylanisole	15	8.57	0.04705	1.99
carbon dioxide	4-methylanisole	15	3.19	0.01437	2.41
carbon dioxide	monoolein	11	13.91	0.07217	1.40
carbon dioxide	myristic acid ethyl ester	16	23.88	0.13220	3.84
carbon dioxide	myristoleic acid	42	16.10	0.08701	4.06
carbon dioxide	myristoleic acid methyl ester	79	10.99	0.04059	9.85
carbon dioxide	naphthalene	83	18.80	0.09308	8.66
carbon dioxide	1-naphthol	11	28.26	0.14034	1.82
carbon dioxide	2-naphthol	16	30.21	0.16301	2.53
carbon dioxide	2-nitroanisole	15	9.94	0.05278	1.63
carbon dioxide	nitrobenzene	15	11.75	0.06177	2.17

Table 1 (*Continued*)

System			TLSM	TLSM_d	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,\text{d}}$	AARD
carbon dioxide	3-nitrotoluene	15	12.84	0.06904	2.74
carbon dioxide	2-nonanone	10	44.20	0.25191	4.21
carbon dioxide	5-nonanone	12	42.00	0.23312	4.95
carbon dioxide	*n*-nonane	5	41.26	0.22243	3.65
carbon dioxide	*n*-octane	5	38.37	0.20280	3.65
carbon dioxide	oleic acid	19	12.15	0.07040	2.52
carbon dioxide	oleic acid ethyl ester	5	11.85	0.05356	5.87
carbon dioxide	oleic acid methyl ester	19	9.19	0.01920	8.59
carbon dioxide	palladium(II) acetylacetonate	125	5.02	0.02298	2.86
carbon dioxide	palmitic acid ethyl ester	17	22.88	0.12236	3.18
carbon dioxide	*n*-pentane	5	20.76	0.09652	3.15
carbon dioxide	2-pentanone	23	18.46	0.09926	2.06
carbon dioxide	3-pentanone	39	18.58	0.09767	1.72
carbon dioxide	*n*-pentylbenzene	31	15.05	0.08136	2.09
carbon dioxide	phenanthrene	19	32.07	0.17684	5.49
carbon dioxide	phenol	109	13.41	0.06924	3.19
carbon dioxide	phenylacetic acid	16	17.71	0.08843	2.01
carbon dioxide	phenylacetylene	15	8.67	0.04421	1.22
carbon dioxide	1-phenyldodecane	15	5.84	0.02988	2.37
carbon dioxide	1-phenylethanol	15	4.81	0.02205	1.84
carbon dioxide	2-phenylethanol	15	5.33	0.02655	2.00
carbon dioxide	2-phenylethyl acetate	15	4.49	0.02441	2.09
carbon dioxide	1-phenylhexane	15	13.96	0.07294	1.95
carbon dioxide	phenylmethanol	15	9.56	0.04883	1.79
carbon dioxide	1-phenyloctane	15	16.15	0.08161	2.57
carbon dioxide	2-phenyl-1-propanol	15	1.82	0.00374	1.73
carbon dioxide	3-phenyl-1-propanol	15	5.52	0.02829	2.17
carbon dioxide	3-phenylpropyl acetate	15	4.78	0.02311	2.56
carbon dioxide	α-pinene	15	17.69	0.09860	3.61
carbon dioxide	β-pinene	15	22.56	0.12156	3.59
carbon dioxide	1-propanol	17	42.27	0.24133	4.99
carbon dioxide	2-propanol	18	12.07	0.06695	3.97
carbon dioxide	*i*-propylbenzene	15	17.95	0.09346	2.23
carbon dioxide	*n*-propylbenzene	34	15.06	0.07363	9.46
carbon dioxide	pyrene	18	26.58	0.12463	2.38

Table 1 (*Continued*)

System			TLSM	TLSM$_d$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,d}$	AARD
carbon dioxide	squalene	5	23.12	0.12635	4.89
carbon dioxide	stearic acid ethyl ester	17	23.20	0.12763	3.45
carbon dioxide	styrene	15	7.25	0.03774	4.10
carbon dioxide	*n*-tetradecane	5	43.49	0.24688	7.77
carbon dioxide	tetrahydrofuran	15	14.86	0.01551	14.70
carbon dioxide	thenoyltrifluoroacetone	15	14.93	0.07265	3.09
carbon dioxide	α-tocopherol	82	22.67	0.12003	1.32
carbon dioxide	toluene	35	12.38	0.05873	4.29
carbon dioxide	triarachidonin	27	21.83	0.12016	3.16
carbon dioxide	trierucin	101	17.30	0.09500	4.99
carbon dioxide	trifluoroacetylacetone	15	17.33	0.09124	1.82
carbon dioxide	1,3,5-trimethylbenzene	24	8.90	0.04718	4.47
carbon dioxide	trinervonin	38	18.94	0.10235	4.11
carbon dioxide	triolein	10	19.81	0.11783	3.48
carbon dioxide	ubiquinone CoQ10	80	20.66	0.10423	2.69
carbon dioxide	*n*-undecane	5	44.60	0.24395	4.47
carbon dioxide	6-undecanone	13	43.52	0.24303	4.89
carbon dioxide	vanillin	15	11.51	0.05836	1.92
carbon dioxide	vitamin K_1	16	34.45	0.19147	2.15
carbon dioxide	vitamin K_3	20	26.71	0.15360	3.69
chlorotrifluoromethane	acetone	10	26.76	-0.14547	5.96
chlorotrifluoromethane	*p*-xylene	8	23.16	-0.12185	11.82
2,3-dimethylbutane	benzene	11	8.76	-0.03830	1.65
2,3-dimethylbutane	naphthalene	9	3.03	0.01329	2.07
2,3-dimethylbutane	phenanthrene	11	8.48	0.04521	2.91
2,3-dimethylbutane	toluene	10	5.35	-0.02904	1.41
ethane	1-octene	6	14.98	0.06902	5.98
ethane	1-tetradecene	9	26.16	0.13806	2.02
sulfur hexafluoride	benzene	9	14.29	-0.03526	8.41
sulfur hexafluoride	benzoic acid	6	12.32	-0.06603	4.99
sulfur hexafluoride	carbon tetrachloride	6	3.24	-0.00543	3.18
sulfur hexafluoride	naphthalene	5	15.96	0.07964	5.47
sulfur hexafluoride	toluene	11	14.36	-0.06356	11.39
sulfur hexafluoride	1,3,5-trimethylbenzene	10	11.16	-0.03742	10.37
sulfur hexafluoride	*p*-xylene	52	9.76	0.03271	7.57

Table 1 (*Continued*)

System			TLSM	TLSM$_d$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,d}$	AARD
		Liquid Systems			
cyclohexane	argon	6	17.80	0.07877	10.21
cyclohexane	benzene	12	6.29	0.01052	6.07
cyclohexane	carbon tetrachloride	6	11.71	0.05711	3.02
cyclohexane	ethane	5	10.48	0.01358	10.22
cyclohexane	ethylene	5	11.37	-0.00840	10.85
cyclohexane	krypton	6	17.71	0.06555	10.23
cyclohexane	methane	6	16.60	-0.09598	7.38
cyclohexane	naphthalene	12	13.91	0.07176	7.66
cyclohexane	phenanthrene	8	16.35	0.06355	6.30
cyclohexane	tetrabutyltin	7	2.50	0.00126	2.48
cyclohexane	tetraethyltin	7	12.09	0.05902	2.90
cyclohexane	tetramethyltin	7	11.59	0.06161	4.55
cyclohexane	tetrapropyltin	6	9.28	0.03986	3.08
cyclohexane	toluene	12	8.92	0.04098	7.90
cyclohexane	1,3,5-trimethylbenzene	12	8.46	0.04290	6.82
cyclohexane	xenon	6	18.04	0.06313	9.40
cyclohexane	*p*-xylene	8	10.80	0.02861	7.62
n-decane	argon	3	11.92	-0.04678	5.80
n-decane	carbon tetrachloride	3	5.31	-0.02285	1.10
n-decane	12-crown-4	4	12.30	-0.06766	3.04
n-decane	15-crown-5	4	13.12	-0.06779	5.28
n-decane	18-crown-6	4	10.88	-0.06504	3.04
n-decane	dicyclohexano-18-crown-6	4	11.25	-0.06038	2.65
n-decane	dicyclohexano-24-crown-8	4	15.81	-0.08447	2.95
n-decane	krypton	3	6.82	-0.01344	5.76
n-decane	tetrabutyltin	4	20.35	-0.09953	0.68
n-decane	tetraethyltin	3	6.41	-0.03082	1.66
n-decane	tetramethyltin	4	10.68	-0.05821	2.03
n-decane	tetrapropyltin	4	11.80	-0.05759	0.52
n-decane	*s*-trioxane	4	13.51	-0.07009	1.72
n-decane	xenon	4	5.35	-0.03224	3.74
n-dodecane	acetone	5	32.27	-0.14932	1.17
n-dodecane	benzene	4	26.82	-0.12653	0.81
n-dodecane	carbon dioxide	9	19.95	-0.09410	9.67

Table 1 (*Continued*)

System			TLSM	$TLSM_d$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,d}$	AARD
n-dodecane	carbon monoxide	9	48.83	-0.23411	9.34
n-dodecane	*n*-decane	5	6.93	-0.03191	2.18
n-dodecane	*n*-hexadecane	5	16.89	0.08490	4.43
n-dodecane	naphthalene	5	4.01	-0.01689	1.77
n-dodecane	*n*-octane	9	6.00	-0.02986	1.47
n-dodecane	*n*-tetradecane	5	6.52	-0.04059	3.70
n-dodecane	toluene	4	18.76	-0.09509	1.48
n-dodecane	1,3,5-trimethylbenzene	4	17.08	-0.08709	1.53
n-dodecane	*m*-xylene	4	10.18	-0.05137	1.15
n-eicosane	carbon dioxide	5	47.87	-0.23808	4.71
n-eicosane	*n*-dodecane	5	39.65	-0.18043	2.29
n-eicosane	*n*-hexadecane	5	14.11	-0.06732	2.23
n-eicosane	*n*-octane	5	48.73	-0.22864	3.11
n-heptane	*n*-decane	5	1.91	0.00657	1.51
n-heptane	*n*-dodecane	5	8.78	0.03617	2.04
n-heptane	*n*-hexadecane	8	21.91	0.11016	2.80
n-heptane	*n*-octane	4	4.28	0.01530	2.12
n-heptane	*n*-tetradecane	5	4.90	0.02093	1.81
n-hexadecane	carbon dioxide	10	37.23	-0.16959	3.11
n-hexadecane	*n*-decane	5	26.21	-0.11191	11.12
n-hexadecane	*n*-dodecane	5	8.58	-0.03193	4.88
n-hexadecane	*n*-octane	10	25.49	-0.09792	8.82
n-hexadecane	*n*-tetradecane	5	13.46	-0.06702	7.32
n-hexane	acetone	5	15.31	-0.06288	2.31
n-hexane	acetonitrile	7	5.84	-0.00058	5.82
n-hexane	benzene	36	8.12	-0.02713	5.49
n-hexane	carbon disulphide	10	13.25	0.05879	4.76
n-hexane	indole	4	5.02	0.01392	3.74
n-hexane	naphthalene	20	9.48	0.04037	6.67
n-hexane	phenanthrene	15	13.37	0.07799	6.54
n-hexane	toluene	28	5.97	-0.01227	5.45
n-hexane	1,3,5-trimethylbenzene	20	5.26	0.00347	5.22
n-hexane	*m*-xylene	5	2.89	0.00241	2.81
n-hexane	*p*-xylene	17	7.72	0.02291	7.25
n-octane	argon	4	16.61	-0.07683	4.00

Table 1 (*Continued*)

System			TLSM	TLSM$_d$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,d}$	AARD
n-octane	benzene	4	8.90	-0.04954	1.66
n-octane	carbon tetrachloride	4	1.79	-0.01144	0.56
n-octane	ethyl benzene	4	10.04	-0.05177	2.04
n-octane	krypton	4	8.09	-0.04556	4.80
n-octane	methane	4	61.17	-0.26878	2.13
n-octane	tetrabutyltin	4	11.62	-0.06694	2.21
n-octane	tetraethyltin	5	5.34	-0.00626	4.74
n-octane	tetramethyltin	4	6.23	-0.02487	1.17
n-octane	tetrapropyltin	4	4.79	-0.02543	1.10
n-octane	toluene	4	8.77	-0.04734	1.75
n-octane	1,3,5-trimethylbenzene	4	12.25	-0.05950	0.24
n-octane	xenon	4	6.26	-0.02914	2.28
n-octane	*o*-xylene	4	2.23	-0.01139	0.73
n-octane	*p*-xylene	4	4.60	0.02264	1.01
propane	1-octene	8	17.78	0.08814	1.92
propane	1-tetradecene	8	25.74	0.13223	1.97
2,2,4-trimethylpentane	benzene	4	31.91	-0.15431	1.65
2,2,4-trimethylpentane	ethylbenzene	4	31.88	-0.15399	1.34
2,2,4-trimethylpentane	toluene	4	27.72	-0.13378	1.64
2,2,4-trimethylpentane	1,3,5-trimethylbenzene	4	34.62	-0.17713	4.27
2,2,4-trimethylpentane	*o*-xylene	4	27.34	-0.12400	2.46
2,2,4-trimethylpentane	*p*-xylene	4	14.73	-0.07543	1.82
Gas Systems					
argon	*i*-butane	8	16.07	-0.08144	1.52
argon	*n*-butane	8	12.81	-0.06433	1.39
argon	ethane	9	4.83	-0.02437	1.35
argon	hydrogen	5	4.96	0.01681	4.44
argon	methane	9	3.07	0.00365	2.97
argon	neon	25	2.13	-0.00474	2.00
argon	propane	9	3.62	-0.01660	1.09
carbon dioxide	ethylene	48	9.61	-0.04759	5.18
carbon dioxide	hydrogen	7	7.92	-0.03864	0.38
carbon monoxide	helium	7	12.47	0.06392	0.21
carbon monoxide	hydrogen	7	0.21	-0.00012	0.20
deuterium	hydrogen	5	12.79	0.07325	2.10

Table 1 (*Contined*)

System			TLSM	$\mathrm{TLSM_d}$	
Solvent (1)	Solute (2)	NDP	AARD	$k_{12,\mathrm{d}}$	AARD
ethane	nitrogen	14	8.37	-0.04068	1.05
ethylene	carbon dioxide	49	7.32	-0.00496	7.27
ethylene	nitrogen	7	6.52	-0.03156	0.39
helium	hydrogen	17	17.55	0.09254	2.33
krypton	argon	6	2.74	-0.01771	1.96
krypton	helium	6	2.59	-0.01227	1.45
krypton	neon	17	13.61	-0.06838	1.95
krypton	xenon	8	5.92	-0.02775	1.97
methane	carbon dioxide	10	1.75	-0.00450	1.64
methane	tetrachloroethene	5	25.79	-0.12146	0.57
neon	deuterium	5	4.51	0.02278	2.46
neon	helium	24	9.26	0.04915	1.64
neon	hydrogen	5	11.44	0.06364	2.00
neon	xenon	6	3.20	-0.01774	0.75
nitrogen	*n*-butane	5	21.41	-0.10324	2.49
nitrogen	helium	8	4.26	0.01727	2.60
nitrogen	hydrogen	29	5.04	0.02783	1.25
nitrogen	methane	7	2.59	0.00393	2.49
nitrogen	propane	6	15.92	-0.08820	2.37
oxygen	helium	8	5.23	0.02530	1.41
oxygen	hydrogen	13	8.46	0.04425	1.26
sulfur hexafluoride	cyclohexane	5	20.82	-0.09742	0.92
sulfur hexafluoride	methylcyclohexane	5	18.34	-0.08403	1.73
tetrafluoromethane	tetrachloroethene	5	7.87	-0.04476	1.70
tetrafluoromethane	1,1,1-trichloroethane	5	1.49	-0.00726	0.78

Taking into account the constants and properties listed in this paper, it is now possible to estimate easily the tracer diffusivity of a large number of systems using $\mathrm{TLSM_d}$ correlation. When $k_{12,\mathrm{d}}$ is unknown, the predictive model should be adopted; nonetheless, if some data points may be found in the literature, the value of $k_{12,\mathrm{d}}$ may be firstly optimized.

In the whole, very good results have been accomplished, as the grand averages shown in Table 2 point out: $\mathrm{AARD(TLSM)} = 15.71\%$ and $\mathrm{AARD(TLSM_d)} = 3.89\%$.

Concerning the equations adopted for comparison, the deviations of the predictive models of Zhu *et al.* [12] and Tyn-Calus [2, 13] are 37.49% and 19.01%, respectively, and the $2-$parameter equation of Dymond-Hildebrand-Batschinsky (DHB) [3-4, 11] presents 3.85%.

Table 2. Percent deviations for each system.

System	NDP	NS	TLSM	TLSM$_d$	Dymond	Zhu *et al.*	Tyn-Calus
Supercritical	4256	168	16.71	3.90	3.79	37.29	16.63
Liquid	601	91	13.91	4.67	5.35	37.18	35.87
Gas	422	37	8.24	2.68	2.33	39.95	–
Total	5279	296	15.71	3.89	3.85	37.49	19.01

The binary parameter, $k_{12,\mathrm{d}}$, seems sufficient to achieve good representations of D_{12} for all systems studied, which emphasizes the reliability of the model. It is worth noting its introduction has diminished significantly the AARDs of TLSM. On the other hand, despite possessing two parameters, the DHB equation exhibits results comparable to those of TLSM$_d$ (AARD = 3.89% *versus* 3.85%). Nonetheless, it is well known their parameters are physically meaningless, which limits its interest to interpolation purposes only [3, 10].

It may be emphasized the good performance achieved for systems whose LJ force constants (energy and diameter) were both calculated using critical constants also estimated. For instance, this is the case of systems containing 1,1′-dimethylferrocene, cobalt(III) acetylacetonate, copper(II) trifluoroacetylacetonate, dibenzo-24-crown-8, ferrocene, $\gamma-$linolenic acid ethyl ester, palladium(II) acetylacetonate, squalene, tetrabutyltin, thenoyltrifluoroacetone, triarachidonin, triolein, ubiquinone CoQ10, vitamins K$_1$ and K$_3$. In the case of these molecules, the unique properties previously known were molecular weight and boiling point. Note that most group contribution methods available to estimate T_c, P_c and V_c do not comprehend metallic atoms like Co, Fe, Pd, Cu, Sn. Hence, the critical constants have been calculated by Klincewicz method [2, 21]. Even so, the AARDs found were surprisingly small for these systems, in the range of 0.52 to 6.27 %.

In Figure 1 the experimental tracer diffusivities of palladium(II) acetylacetonate and β-carotene in carbon dioxide have been plotted against density, along with the results provided by TLSM$_d$ correlation. These systems were selected to illustrate the behaviour of the model over wide density ranges for systems whose LJ parameters were estimated, and in the severe situation where even the critical constants were also unknown. As Figure 1 points out, results are in good agreement with experimental data.

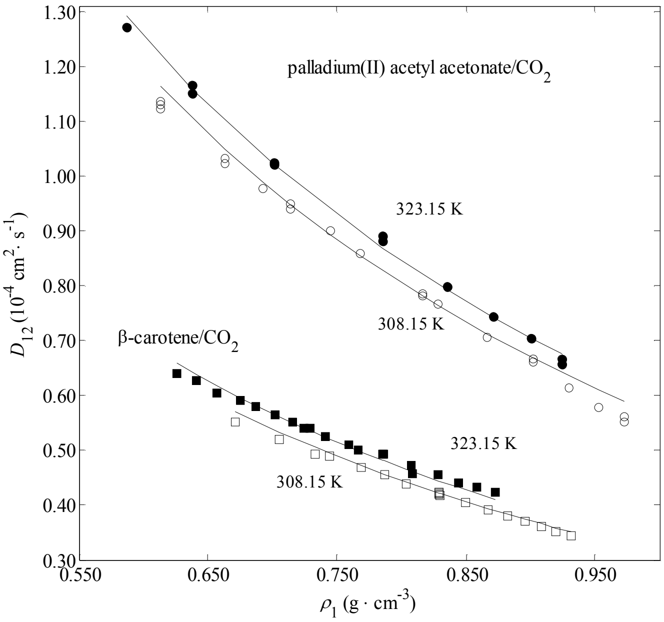

Figure 1. Experimental tracer diffusivities of palladium(II) acetylacetonate and β-carotene in carbon dioxide, plotted against solvent density. The results provided by TLSM$_d$ correlation also are shown.

4.PI.6. Conclusions

In this work the largest database of tracer diffusion coefficients has been compiled, embodying 296 systems and 5279 points, in order to enlarge the applicability of the previously published TLSM and TLSM$_d$ models (with 0 and 1 parameters, respectively). The input data are the molecular weights and Lennard-Jones diameters and energies of the solute and solvent, and one binary interaction parameter of the system. All of them were calculated/optimized in this Research Note. The deviations found (AARD = 3.89%) point out the TLSM$_d$ model provides reliable and very good estimates of D_{12}.

Nomenclature

AARD	Average absolute relative deviation, $\mathrm{AARD} = (100/\mathrm{NDP}) \times \sum_{i=1}^{\mathrm{NDP}} \left\| D_{12,i}^{\mathrm{calc}} - D_{12,i}^{\mathrm{exp}} \right\| / D_{12,i}^{\mathrm{exp}}$, %
D	Diffusion coefficient, $\mathrm{cm^2 \cdot s^{-1}}$
DHB	Dymond-Hildebrand-Batschinski
$k_{12,\mathrm{d}}$	Binary interaction parameter
LJ	Lennard-Jones
TLSM	Tracer Liu-Silva-Macedo equation
M	Molecular weight, $\mathrm{g \cdot mol^{-1}}$
N_a	Avogadro constant, $6.0221367 \times 10^{23}\ \mathrm{mol^{-1}}$
NDP	Number of data points
NS	Number of systems
P	Pressure, bar
$\Re_\mathrm{g}$	Universal gas constant, $8.3144\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
T	Temperature, K

Greek Letters

$\varepsilon / k_\mathrm{B}$	Lennard-Jones energy parameter, K
σ	Lennard-Jones diameter, Å
ρ	Number density, $\mathrm{cm^{-3}}$

Subscripts

1	Solvent
2	Solute
12	Binary property
c	Critical property
eff	Refers to the effective hard sphere diameter
r	Reduced property (using critical constants)

Superscripts

$*$	Reduced property (using LJ parameters)

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Paper II

Adapted from

New Models for Tracer Diffusion Coefficients of Hard Sphere and Real Systems: Application to Gases, Liquids and Supercritical Fluids

Journal of Supercritical Fluids, **2011**, 55, 898–923.

Abstract

In this work very accurate expressions for the tracer diffusion coefficient of hard sphere (HS) and real systems are proposed. The new HS model depends explicitly on the reduced density of solvent, and on the ratios of the diameters and masses of solute and solvent. It provides a very good representation of molecular dynamics data taken from literature: average absolute relative deviation, AARD = 4.44%. With respect to real fluids, the proposed model was developed according to Rice and Gray approach, and is based on the previous HS equation. The model involves only one parameter and requires temperature, solvent density, and solute and solvent molecular weight and LJ force constants (these are estimated as function of the critical temperature and molar volume). Results calculated for 309 systems and 5341 data points gave rise to AARD = 4.26%, and shows the model interprets equally well the diffusive phenomena of gases, liquids and SCFs.

4.PII.1. Introduction

Infinite dilution diffusion coefficients (D_{12}) are key transport properties in project and design of challenging chemical reactors and separation processes. For instance, unit operations based on supercritical fluid extraction frequently requires diffusivities difficult to grasp from experimental data, or to update to specific temperature and pressure conditions. Expressions for their calculation with limited available data constitute an ambitious objective. With such purpose, several models have appeared targeting specific temperature and pressure ranges, and fluid physical states [1-3]. More recently, wide range application models were proposed to predict tracer diffusion coefficients, namely those by Liu *et al.* [4], Liu and Ruckenstein [5], and Zhu *et al.* [6], whose validation involved between 74 to 120 binary systems (1033 to 1443 data points) with average absolute relative deviations (AARDs) between 8.42% and 17.31%.

In this work we aim to develop new models for the tracer diffusivities of hard sphere (HS) and real fluids. Accordingly, an empirical correlation for $D_{12,\mathrm{HS}}$ is firstly devised on the basis of molecular dynamics (MD) data available in the literature for the HS fluid. Then, a new equation for LJ tracer diffusivities, $D_{12,\mathrm{LJ}}$, is obtained by taking into account the Rice and Gray's approach [5, 7-9]. Finally, an adjustable interaction binary parameter is embodied in this LJ model, in order to extend its application to real systems. The validation of our model for real molecules has been accomplished with the largest database ever compiled, which comprehends 309 systems and 5341 data points.

4.PII.2. Theoretical Approach

The theoretical path adopted in this essay to develop the desired tracer diffusion models is shown in Figure 1. Our approach considers four stages: it starts with ideal gases and passes to hard spheres by correcting Enskog theory; by introducing an attractive contribution and adopting effective hard sphere diameters, a LJ model arises from the HS model; finally, LJ model is extended to real systems.

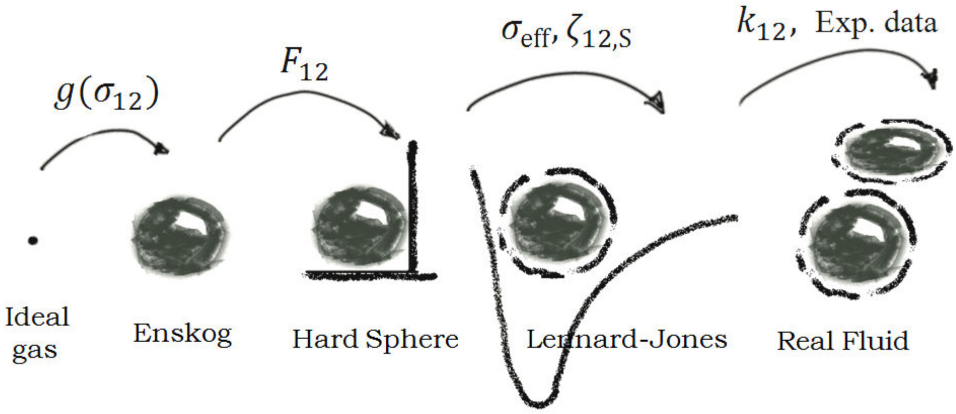

Figure 1. Steps for the development of the new tracer diffusion coefficient model for real systems.

4.PII.2.1 Ideal gas

The diffusion coefficient of dilute gases (*i.e.* in the limit of zero density), D_{12}^0, may be estimated from the rigorous kinetic theory by [2, 9]:

$$\rho_1^0 D_{12}^0 = \frac{3}{8\sigma_{12}^2}\left(\frac{k_B T}{2\pi m_{12}}\right)^{1/2} \tag{1}$$

where superscript "0" stands for dilute gas, subscripts "1" and "2" denote solvent and solute, respectively, ρ_1 is number density, k_B is Boltzmann constant, T is absolute temperature, m_{12} is the reduced mass of the system, and σ_{12} is the distance between the centers of the molecules at collision. The values of σ_{12} and m_{12} are obtained from the individual molecular diameters and masses by:

$$\sigma_{12,\mathrm{LJ}} = \frac{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}{2} \tag{2}$$

$$m_{12} = \frac{m_1\, m_2}{m_1 + m_2} = \frac{M_1\, M_2}{N_\mathrm{a}\left(M_1 + M_2\right)} \tag{3}$$

Eq. (1) is valid for monatomic gases and has to be modified if molecules have internal structure. Also, it is not applicable to dense gases and liquids since it is based upon the Boltzmann equation for the distribution function.

4.PII.2.2 Enskog fluid

A kinetic theory for transport coefficients of a dense HS system has been developed by Enskog [10], who considered that the molecular diameters are no longer negligible compared with interparticle distance, and modified the collision frequency in the fluid by the unlike pair radial distribution function at contact, $g(\sigma_{12})$. The Enskog equation for the tracer diffusion coefficient is:

$$\frac{\rho_1\, D_{12,\mathrm{E}}}{\rho_1^0\, D_{12}^0} = \frac{1}{g(\sigma_{12})} \tag{4}$$

In this work $g(\sigma_{12})$ is calculated as proposed by Mansoori *et al.* [11]:

$$g(\sigma_{12}) = \frac{1}{(1-\varphi_1)^3}\left(1-\varphi_1+\frac{2\varphi_1}{1+\sigma_1/\sigma_2}\right)\left(1-\varphi_1+\frac{\varphi_1}{1+\sigma_1/\sigma_2}\right) \tag{5}$$

where φ_1 is the HS packing fraction of the solvent, which for N_1 spheres occupying a volume V is given by:

$$\varphi_1 = \frac{N_1\,\pi\,\sigma_1^3}{6V} = \frac{\pi}{6}\rho_1\,\sigma_1^3 = \frac{\pi}{6}\rho_1^* \tag{6}$$

$\rho_1^* \equiv \rho_1 \sigma_1^3$ is the well known reduced number density.

4.PII.2.3 Hard sphere fluid

The Enskog theory is based on the molecular chaos approximation, and therefore it is not applicable over large density range. The errors introduced neglecting correlated motions between core collisions, which gives rise to both backscattering and vortex flow effects, have been studied in computer simulations for systems of a single test particle in a solvent, for selected size and mass ratios, to assess the necessary correction [2, 9]. The HS tracer diffusivity is usually written as a modification of the Enskog theory, by introducing a correction factor hereafter denoted by F_{12}:

$$D_{12,\mathrm{HS}} = \left(\frac{D_{12,\mathrm{HS}}}{D_{12,\mathrm{E}}} \right) D_{12,\mathrm{E}} = F_{12}\, D_{12,\mathrm{E}} \tag{7}$$

This correction factor depends on the reduced density of the solvent, and on the size and mass ratios, so one may write:

$$F_{12} = F_{12}\left(\rho_1^*, \sigma_2/\sigma_1, m_2/m_1\right) \tag{8}$$

As shown by Alder *et al.* [12], the dependence of F_{12} is complex: at low densities, it increases with increasing σ_2/σ_1 when $m_2/m_1 = 1.00$, while diminishes with increasing σ_2/σ_1 for $m_2/m_1 \leq 0.10$; at high densities, F_{12} always decreases as σ_2/σ_1 increases. Additionally, it must satisfy the following four restrictions:

i) For equal diameters and masses, F_{12} reduces to the self-diffusion correction factor, F_{11}, for which several good correlations are available [8, 13-15]:

$$\lim_{\substack{\sigma_1/\sigma_2 \to 1 \\ m_1/m_2 \to 1}} F_{12} = \frac{D_{11,\mathrm{HS}}}{D_{11,\mathrm{E}}} = F_{11}\left(\rho_1^*\right) \tag{9}$$

ii) At low density the Enskog theory has to be recovered:

$$\lim_{\rho_1^* \to 0} F_{12}\left(\rho_1^*, \sigma_1/\sigma_2, m_1/m_2\right) = 1 \tag{10}$$

iii) At low density, the self-diffusion correction factor derived from Eq. (9), F_{11}, must satisfy Enskog theory:

$$\lim_{\rho_1^* \to 0} F_{11}\left(\rho_1^*\right) = 1 \tag{11}$$

iv) The self-diffusion correction factor derived from Eq. (9), F_{11}, should vanish at an intrinsic high density ρ_s^*:

$$\lim_{\rho_1^* \to \rho_s^*} F_{11}\left(\rho_1^*\right) = 0 \tag{12}$$

A new F_{12} explicit and very accurate expression is proposed in the next section of this paper. Results will be compared with those provided by the well known models of Sung and Stell [16], Eaton and Akgerman [17], Easteal and Woolf [18], and Sun and Chen [19], whose equations are compiled in Section 4.PII.A.

4.PII.2.4 Lennard-Jones fluid

The LJ tracer diffusion coefficient is obtained by introducing an attractive contribution and an effective diameter (σ_{eff}) on the HS model. In this essay, the first effect is taken into account in the framework of Rice and Gray [5, 7-9] approach, which states that:

$$D_{12,\mathrm{LJ}} = \frac{k_{\mathrm{B}}\,T}{\zeta_{12,\mathrm{R}} + \zeta_{12,\mathrm{S}}} \tag{13}$$

where $\zeta_{12,\mathrm{R}}$ is a repulsive friction coefficient, and $\zeta_{12,\mathrm{S}}$ is a soft attraction friction coefficient. From Eqs. (4) and (7) it is clear that:

$$\zeta_{12,\mathrm{R}} = \frac{8}{3}\rho_1\,\sigma_{12,\mathrm{eff}}^2\sqrt{2\,\pi\,m_{12}\,k_{\mathrm{B}}\,T}\,\frac{g\left(\sigma_{12,\mathrm{eff}}\right)}{F_{12}} \tag{14}$$

With respect to $\zeta_{12,\mathrm{S}}$, an expression due to Ruckenstein and Liu [8] is chosen:

$$\zeta_{12,S} = \frac{8}{3}\rho_1\,\sigma_{12,\mathrm{eff}}^2\sqrt{2\,\pi\,m_{12}\,k_\mathrm{B}\,T}\,\frac{0.4}{T_{12}^{*1.5}} \tag{15}$$

When Eqs. (14) and (15) are substituted in Eq. (13), the following explicit $D_{12,\mathrm{LJ}}$ model is found:

$$D_{12,\mathrm{LJ}} = \frac{k_\mathrm{B}\,T}{\frac{8}{3}\rho_1\,\sigma_{12,\mathrm{eff}}^2\left(2\,\pi\,m_{12}\,k_\mathrm{B}\,T\right)^{1/2}\left[\frac{g\left(\sigma_{12,\mathrm{eff}}\right)}{F_{12}} + \frac{0.4}{T_{12}^{*1.5}}\right]} \tag{16}$$

The effective diameter of the system, $\sigma_{12,\mathrm{eff}}$, is computed by the expression of Ben-Amotz and Herschbach (BAH) according to Boltzmann criterion [9, 20-21]:

$$\sigma_{12,\mathrm{eff}} \equiv \sigma_{12,\mathrm{BAH}} = 1.1532\,\sigma_{12,\mathrm{LJ}}\left[1+\left(1.8975\,T_{12}^*\right)^{1/2}\right]^{-1/6} \tag{17}$$

Moreover, it is worth noting that $g(\sigma_{12,\mathrm{eff}})$ imply the calculation of the both effective diameters, $\sigma_{1,\mathrm{eff}}$ and $\sigma_{2,\mathrm{eff}}$ and also $\varphi_{1,\mathrm{eff}} = \frac{\pi}{6}\rho_1\sigma_{1,\mathrm{eff}}^3$, as Eqs. (5) and (6) clearly show. In this case, the following single component analogue is adopted:

$$\sigma_{i,\mathrm{eff}} \equiv \sigma_{i,\mathrm{BAH}} = 1.1532\;\sigma_{i,\mathrm{LJ}}\left[1+\left(1.8975\;T_i^*\right)^{1/2}\right]^{-1/6} \tag{18}$$

The implied reduced temperatures are:

$$T_i^* \equiv \frac{k_\mathrm{B}T}{\varepsilon_{i,\mathrm{LJ}}} \qquad T_{12}^* \equiv \frac{k_\mathrm{B}T}{\varepsilon_{12,\mathrm{LJ}}} \tag{19}$$

and the binary LJ diameter and energy are evaluated by the classical Lorentz-Berthelot combining rules:

$$\sigma_{12,\mathrm{LJ}}=\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2}$$

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}}=\sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right)\times\left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)} \tag{20}$$

The individual LJ parameters are calculated as functions of the critical temperature and molar volume of each component [8-9] by, respectively:

$$\frac{\varepsilon_{i,\mathrm{LJ}}}{k_\mathrm{B}}(\mathrm{K})=\frac{T_{\mathrm{c},i}}{1.2593}$$

$$\sigma_{i,\mathrm{LJ}}(\mathrm{cm})=0.7889\times10^{-8}\,V_{\mathrm{c},i}^{1/3} \tag{21}$$

At this moment it is important to emphasize that the calculation of $D_{12,\mathrm{LJ}}$ only depends on the existence of a good model for F_{12}.

4.PII.2.5 Real fluids

In this work, the model for tracer diffusivities of real systems is grafted onto former Eq. (16), by just introducing an adjustable binary parameter k_{12} in the diameter combining rule, akin to a thermodynamic binary correction. This model will be henceforth identified by LJ-1. Accordingly, σ_{12} is now given by:

$$\sigma_{12,\mathrm{LJ}}=\left(1-k_{12}\right)\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \tag{22}$$

This tiny modification will allow us to reach excellent results for gaseous, supercritical and liquid systems without further complexity, as it consists on the introduction of only one fitted parameter for all density and temperature conditions of any system. Such fact reveals that the k_{12} goes through the real interpretation of the diffusive phenomenon, similarly to thermodynamic binary corrections. It is well known that mixtures of hard spheres, whose components interact by a hard-core potential diameter given by Eq. (2), are possibly deprived of typical phenomena of fluid mixtures, such as demixing or partial mixing of the components. It is worth noting that the k_{12} parameter was introduced in the diameter combining rule (Eq. (22)), although comparable results could be obtained by correcting Eq. (20) instead, as has been demonstrated elsewhere [4, 9]. Moreover, in this way the effect of k_{12} is limited to the $\sigma^2_{12,\mathrm{eff}}$ term on the denominator of Eq. (16), which simplifies enormously the required optimizations to determine their values from experimental data.

4.PII.3. New Hard Sphere Correction Factor, F_{12}

In this section it will be presented the new expression for F_{12} proposed in this work, whose final objective is to embody Eq. (16) for the LJ tracer diffusivities, later extended to real fluids. Our model is a simple empirical and explicit expression that satisfies all theoretical restrictions imposed by Eqs. (9) – (12):

$$F_{12} = \frac{F_{11} + \rho_1^{*1.7}\left[a\ln(\sigma_2/\sigma_1) + b\ln^2(\sigma_2/\sigma_1) + c\ln(m_2/m_1)\right]}{1 + \rho_1^{*3.0}\left[d\ln(\sigma_2/\sigma_1)\right]^2} \tag{23}$$

This model arrived after an extensive search carried out with statistical TableCurve 3D® software followed by a modification. Using TableCurve 3D®, equation no 1204 (of rational type with logarithmic variable dependence) gave rise to the best results from the huge set of empirical equations of its database. As described by TableCurve 3D® user manual it «fits 310 polynomials, 300 rationals, scans 453.696.714 selective subset equations fitting up to 36.582 of them». Afterwards, the equation thus obtained was modified to refine the solvent density influence upon F_{12}. Accordingly, coefficients *a*, *b*, *c* and *d* were made linearly dependent on ρ_1^*:

$$\begin{cases} a = -1.676382\,\rho_1^* + 1.638561 \\ b = -8.516830\,\rho_1^* + 8.631536 \\ c = -1.320347\,\rho_1^* + 1.351067 \\ d = -5.062546\,\rho_1^* + 5.409662 \end{cases} \tag{24}$$

The embodied self-diffusion factor, F_{11} , is calculated by the simple and very accurate expression due to Ruckenstein and Liu [8]:

$$F_{11} = 1 + 0.94605\rho_1^{*1.5} + 1.4022\rho_1^{*3} - 5.6898\rho_1^{*5} + 2.6626\rho_1^{*7} \qquad (25)$$

The constants of the linear relationships in Eq. (24) were optimized using 43 MD data points of Herman and Alder [22] and Alder *et al.* [12] for the HS system, in the following ranges: $\rho_1^* = 0.4714 - 0.9428$, $m_2/m_1 = 0.01 - 4.00$, and $\sigma_2/\sigma_1 = 0.25 - 1.00$. Such optimization was accomplished using fminsearch function of Matlab 2006b®; the objective function adopted was the average absolute relative deviation, $\mathrm{AARD}\ (\%) = (100/\mathrm{NDP}) \times \sum_{i=1}^{\mathrm{NDP}} \left| \left(F_{12,i}^{\mathrm{calc}} - F_{12,i}^{\mathrm{MD}}\right) / F_{12,i}^{\mathrm{MD}} \right|_i$.

The representation accomplished by Eqs. (23) − (25) is shown graphically in Figure 2 for two different reduced densities, 0.4714 (middle density) and 0.8839 (high density). It is possible to observe the good fitting provided by the new F_{12} expression, even in the steepest descent region. It is notorious the strong dependence of F_{12} with σ_2/σ_1 ratio when density increases. The average absolute relative deviation found confirms such finding since it reaches only AARD = 4.44% (see Table 1).

The performance of the proposed F_{12} model has been compared with that achieved by four well known models taken from literature, namely Sung and Stell [16], Eaton and Akgerman [17], Easteal and Woolf [18], and Sun and Chen [19]. A concise description of these models is given in Appendix A (Section 4.PII.A). From Table 1 it may be concluded that our model performs undoubtedly better, since the remaining four deviations are much higher: $\mathrm{AARD}_{\text{this work}} = 4.44\%$ against $\mathrm{AARD}_{\text{Sung-Stell}} = 63.89\%$, $\mathrm{AARD}_{\text{Eaton-Akgerman}} = = 67.78\%$, $\mathrm{AARD}_{\text{Easteal-Woolf}} = 18.20\%$, and $\mathrm{AARD}_{\text{Sun-Chen}} = 24.46\%$. In Figure 3 these five models are plotted together with MD data of Alder *et al.* [12] in the following way: $F_{12} = F_{12}(\rho_1^*)$, $F_{12} = F_{12}(m_2/m_1)$, and $F_{12} = F_{12}(\sigma_2/\sigma_1)$. Taking into account Figure 3.a one concludes that the expressions of Sun and Chen [19], and Eaton and Akgerman [17] break the zero density constraint and provide raw quantitative agreement with MD data in the middle density range.

The wrong behaviour offered by these two models is also reinforced in Figure 3.b, where m_2/m_1 is the independent variable, and $\rho_1^* = 0.4714$ and $\sigma_2/\sigma_1 = 1.00$.

From Figure 3.c, where F_{12} is graphed against diameter ratio for $\rho_1^* = 0.9428$ and $m_2/m_1 = 0.01$, it is possible to conclude that the theory of Sung and Stell [16] do presents a noticeable wrong trend, since F_{12} increases while data points decrease. Additionally, the calculated results for Easteal and Woolf [18] are poor in the low and middle density regions, what is also illustrated in Figure 3.a. In the whole, all models from literature exhibit outstanding deficiencies, whereas the results achieved by our model are very accurate for all representations and ranges shown. Such good performance certainly dues to the impositions stressed on Eq. (23) and also to the number of parameters involved in Eq. (24) which is superior to the remaining models (see Section 4.PII.A).

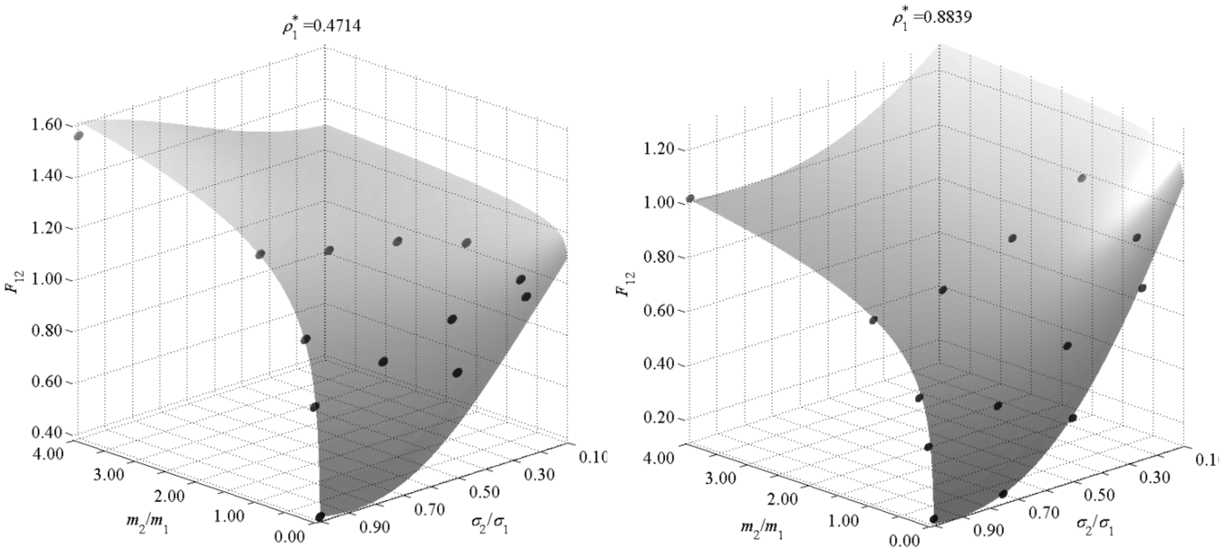

Figure 2. F_{12} correction factor proposed in this work for the calculation of HS tracer diffusion coefficients, given by Eq. (23) against size and mass ratios, and for: a) $\rho_1^* = 0.4714$, and b) $\rho_1^* = 0.8839$; (●) MD data from Herman and Alder [22] and Alder *et al.* [12].

Table 1. Calculated deviations for the F_{12} models studied in this work.

Model	This work (Eqs. (23) – (25))	Sung and Stell (Eqs. (A.1) – (A.5))	Eaton and Akgerman (Eqs. (A.6) – (A.9))	Easteal and Woolf (Eqs. (A.10) and (A.11))	Sun and Chen (Eq. (A.12))
AARD (%)	4.44	63.89	67.78	18.20	24.46

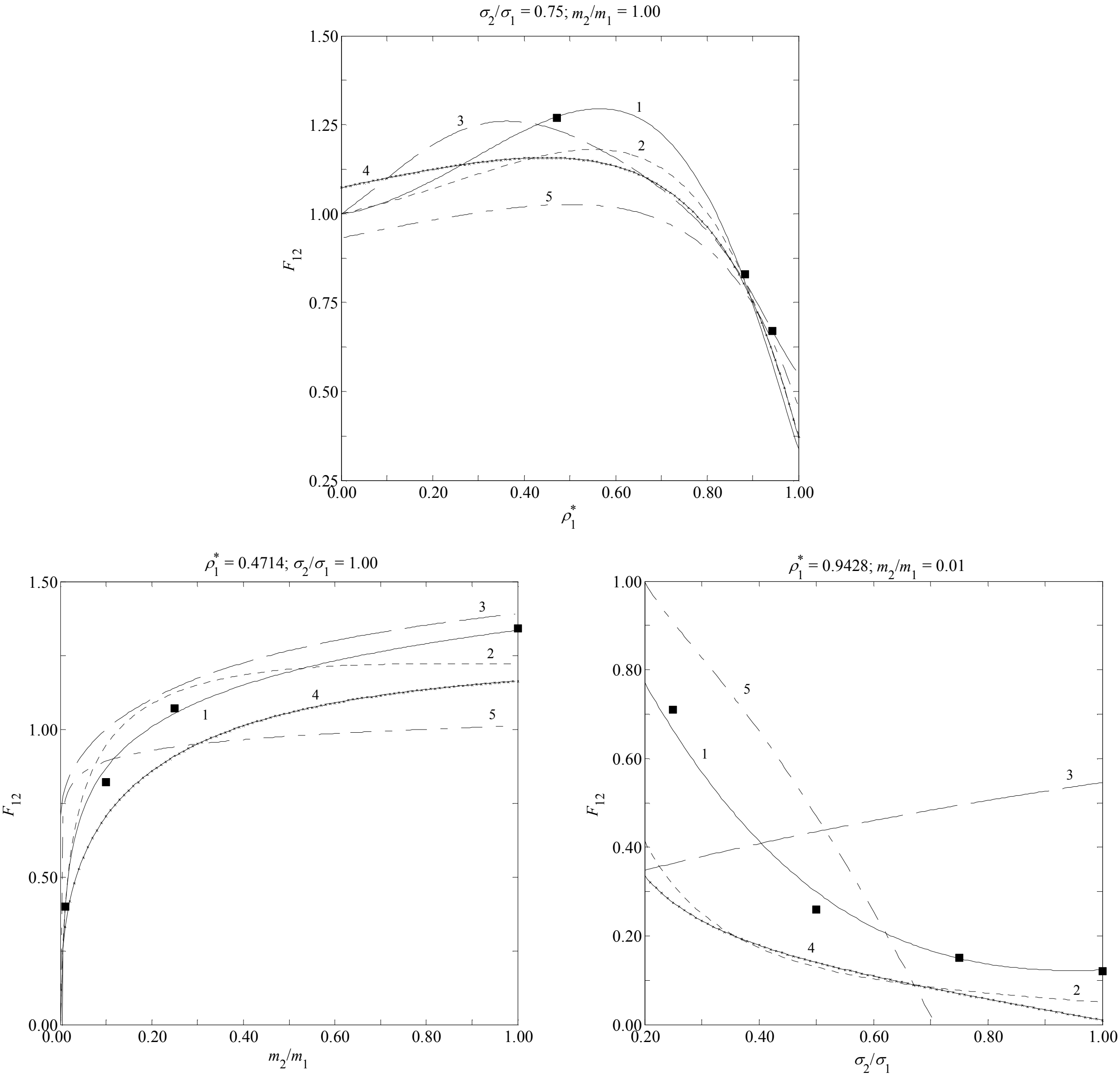

Figure 3. F_{12} correction factors of the HS tracer diffusion coefficient plotted against: a) solvent reduced density ($\sigma_2/\sigma_1 = 0.75$, $m_2/m_1 = 1.00$), b) molecular weight ratio ($\rho_1^* = 0.4714$, $\sigma_2/\sigma_1 = 1.00$), c) molecular size ratio ($\rho_1^* = 0.9428$, $m_2/m_1 = 0.01$). Legend: (■) MD data of Alder *et al.* [12]; 1 – this work, Eqs. (23) – (25); 2 – Easteal and Woolf [18]; 3 – Sung and Stell [16]; 4 – Sun and Chen [19]; 5 – Eaton and Akgerman [17].

4.PII.4. New Tracer Diffusion Coefficient Model for Real Systems

As has been mentioned above, the new model proposed in this work for the limiting mutual diffusion coefficients of real substances (LJ-1) is based on Eq. (16) for the LJ fluid, by introducing an interaction parameter k_{12} in the diameter combining rule, Eq. (22). Accordingly, it is possible to fit k_{12} to experimental data available in the literature for any system.

4.PII.4.1 Database

In this work it has been compiled the largest database ever used: 309 systems performing 5341 points, covering gas (37 sytems/422 points), liquid (101 systems/641 points) and supercritical (171 systems/4278 points) mixtures. Database contains diffusivities collected from open literature. It is evident the increasing number of publications for supercritical systems in comparison to gases and liquids, especially during last decade, which confirms the growing interest on green separation and reaction techniques. Table 3.1 (Chapter 3) contains the systems studied, the reduced ranges of temperature, pressure, and solvent density for each system (reduction performed with critical constants), number of data points (NDP), and data sources. As much as possible, all published data were used. However, systems with data available only in graphical form have been rejected.

4.PII.4.2 Data for the calculations

In Table 3.2 (Chapter 3) the name, molecular formula, CAS number, molecular weight, critical constants (T_c, P_c and V_c), and molar volume at normal boiling point (V_{bp}) are listed for all molecules involved in calculations. All data sources are identified.

4.PII.4.3 Results and discussion

Table 2 shows a compilation of the detailed results obtained with our model and the equations adopted for comparison, namely: the hydrodynamic expressions of Wilke-Chang (WC) [1, 3, 23], Tyn-Calus (TC) [1, 24], Scheibel (Sch) [1, 3, 25] and Reddy-Doraiswy (RD) [1, 3, 26], with zero parameters; the predictive He-Yu-Su model (HYS) [27] (specific for supercritical systems); the predictive equation of Zhu *et al.* (Zhu) [6]; and Dymond correlation (DHB) [2, 9, 28] (2 parameters). The full expressions of these models may be found in Appendix B (see Section 4.PII.B). Global results were compiled in Table 3. With regard to the calculation procedure and results, one may detach the following comments:

(1) The proposed LJ-1 model involves only one parameter k_{12}. The required input data are temperature, solvent density, and, for both components, the molecular weight and

Table 2. Calculated Results.

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
					Supercritical Systems								
2,3-dimethylbutane	benzene	11	-0.03812	1.25	0.9661	70.08	1.56	7.93	4.46	75.95	81.84	156.21	56.59
2,3-dimethylbutane	naphthalene	9	-0.01904	1.17	0.7527	66.74	1.75	2.41	2.76	65.82	85.96	119.78	68.14
2,3-dimethylbutane	phenanthrene	11	-0.02096	1.30	0.5871	54.23	1.53	5.23	2.49	61.35	90.49	104.02	77.61
2,3-dimethylbutane	toluene	10	-0.03062	1.32	0.9458	77.91	1.79	4.82	4.75	72.49	84.58	140.62	62.29
carbon dioxide	1,1,1,5,5,5-hexafluoroacetylacetone	15	-0.01094	4.31	1.1460	11.05	4.36	23.39	10.10	18.95	27.98	33.14	91.59
carbon dioxide	1,1'-dimethylferrocene	68	0.01041	2.44	1.2835	11.85	3.67	29.12	17.13	12.16	20.35	25.53	79.91
carbon dioxide	1,2-dichlorobenzene	15	0.06039	2.12	1.5427	16.61	2.07	10.51	9.25	6.89	11.69	19.05	65.11
carbon dioxide	1,2-diethylbenzene	15	0.08839	2.17	1.3663	15.06	2.61	11.78	3.30	6.19	6.01	6.09	61.99
carbon dioxide	1,3,5-trimethylbenzene	24	0.04073	4.97	1.2531	11.01	4.29	13.33	10.57	7.27	14.10	16.95	71.51
carbon dioxide	1,3-divinylbenzene	15	0.08070	1.57	1.5589	18.35	1.39	12.10	2.34	3.74	7.74	10.19	62.36
carbon dioxide	1,4-diethylbenzene	15	0.08194	2.41	1.3865	15.72	4.06	11.17	3.56	5.65	6.72	6.97	63.10
carbon dioxide	15-crown-5	29	0.11868	5.30	0.9986	1.19	5.98	21.17	13.43	7.85	12.64	11.20	74.02
carbon dioxide	1-naphthol	11	0.14034	1.82	2.1460	24.53	0.88	9.22	18.59	5.77	0.39	5.67	48.49
carbon dioxide	1-phenyldodecane	15	0.08194	2.33	0.9485	17.21	3.14	26.54	16.09	6.96	18.09	7.99	94.23
carbon dioxide	1-phenylethanol	15	0.03349	1.84	1.3428	14.22	3.15	11.15	7.66	10.31	17.97	23.56	75.96
carbon dioxide	1-phenylhexane	15	0.09175	2.10	1.2534	16.08	2.71	14.59	4.98	7.52	7.80	5.06	68.63
carbon dioxide	1-phenyloctane	15	0.09793	2.62	1.1894	16.53	3.65	20.79	3.77	8.65	8.49	3.91	72.00
carbon dioxide	1-propanol	17	0.03343	5.04	1.3448	-10.04	3.00	8.71	10.36	15.43	11.60	33.81	56.46
carbon dioxide	2,2,4,4-tetramethyl-3-pentanone	9	0.21054	2.52	3.0352	29.08	0.76	24.62	33.00	27.01	21.41	18.31	17.70
carbon dioxide	2,3-dimethylaniline	15	0.00436	2.26	1.2259	13.77	2.38	12.08	16.97	16.04	24.54	29.92	86.17

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^3 \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	2,3-dimethylnaphthalene	3	0.09695	1.02	1.5361	21.43	1.08	10.35	1.25	3.66	8.29	7.70	66.40
carbon dioxide	2,4-dimethyl-3-pentanone	8	-0.04379	3.06	1.7583	25.46	2.33	27.67	15.38	29.97	34.48	46.54	96.69
carbon dioxide	2,4-dimethylphenol	15	0.03564	3.34	1.1649	8.33	3.63	11.95	8.03	9.42	16.90	22.58	74.26
carbon dioxide	2,6-dimethylaniline	15	0.03267	3.36	1.1330	8.66	3.34	11.78	12.35	11.47	19.64	24.80	78.84
carbon dioxide	2,6-dimethylnaphthalene	6	0.08942	4.52	1.1736	10.78	4.24	15.38	5.28	7.15	9.26	8.88	67.76
carbon dioxide	2,7-dimethylnaphthalene	6	0.09355	4.35	1.5069	19.63	4.50	11.91	4.68	6.91	6.00	5.64	60.69
carbon dioxide	2-bromoanisole	15	0.02773	2.14	1.2561	12.79	3.66	10.23	11.27	16.52	23.81	30.64	83.97
carbon dioxide	2-butanone	38	0.07918	1.62	2.0672	16.91	2.60	9.83	3.98	5.38	5.39	10.33	38.58
carbon dioxide	2-ethyltoluene	15	0.07968	3.41	1.4172	14.72	3.76	9.30	5.62	8.95	4.63	4.63	53.63
carbon dioxide	2-fluoroanisole	15	0.00637	2.12	1.3944	14.19	2.58	9.93	3.35	18.48	22.85	33.51	79.91
carbon dioxide	2-heptanone	11	0.21051	3.88	3.4792	32.29	1.83	22.02	26.86	30.11	24.33	21.82	13.71
carbon dioxide	2-methylanisole	15	0.02917	2.25	1.3055	12.12	2.79	9.69	5.18	9.67	16.19	23.02	72.34
carbon dioxide	2-naphthol	16	0.14634	2.84	1.9948	21.27	1.73	6.52	23.33	7.84	2.46	5.02	45.23
carbon dioxide	2-nitroanisole	15	0.03639	1.86	1.2984	15.75	2.39	10.88	3.48	11.47	20.75	24.69	81.49
carbon dioxide	2-nonanone	10	0.24779	3.53	2.8331	29.00	2.35	25.05	29.36	35.76	27.22	28.14	12.37
carbon dioxide	2-pentanone	23	0.07783	2.05	1.7185	12.62	2.52	7.78	4.35	4.45	4.27	13.04	47.94
carbon dioxide	2-phenyl-1-propanol	15	0.02865	2.00	1.2825	15.24	2.64	15.83	9.53	9.72	19.88	22.66	81.11
carbon dioxide	2-phenylethanol	15	0.02805	1.91	1.3652	15.18	3.03	10.31	8.49	12.10	19.59	25.60	78.14
carbon dioxide	2-phenylethyl acetate	15	0.03280	2.68	1.1080	13.22	3.06	13.89	9.82	8.63	22.22	21.45	87.91
carbon dioxide	2-propanol	18	0.05193	4.07	1.5735	-1.37	2.21	7.42	6.43	9.57	6.96	26.96	48.70
carbon dioxide	3-ethyltoluene	15	0.08838	3.69	1.4175	14.91	4.00	9.82	6.07	11.68	5.28	5.07	50.98

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	3-nitrotoluene	15	0.07620	2.25	1.3849	14.90	3.96	9.58	2.86	4.00	8.67	11.30	64.09
carbon dioxide	3-pentanone	39	0.10192	1.45	2.0419	19.27	2.03	9.04	4.22	9.48	6.20	3.73	38.28
carbon dioxide	3-phenyl-1-propanol	15	0.04329	1.66	1.5158	20.64	2.28	9.50	7.82	6.21	16.54	18.65	76.57
carbon dioxide	3-phenylpropyl acetate	15	0.03716	3.39	1.0565	12.96	3.37	14.86	9.79	7.12	21.63	18.93	89.00
carbon dioxide	4-ethyltoluene	15	0.06296	3.10	1.4780	17.40	3.07	8.89	8.12	7.46	4.10	4.86	56.37
carbon dioxide	4-heptanone	9	0.24990	1.67	3.1752	27.31	0.47	29.62	32.43	36.53	30.93	29.03	4.11
carbon dioxide	4-methylanisole	15	-0.00839	1.84	1.3473	16.11	3.21	12.16	12.63	17.52	24.50	31.83	84.67
carbon dioxide	5-nonanone	12	0.22800	4.07	3.0575	32.15	1.10	25.83	26.31	34.31	25.24	26.49	15.74
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	0.08648	2.10	1.6033	22.88	3.02	13.60	3.34	8.45	5.81	3.65	64.73
carbon dioxide	6-undecanone	13	0.25178	3.76	2.8101	31.76	2.53	27.76	28.03	38.53	27.40	30.77	14.91
carbon dioxide	arachidonic acid (AA)	75	0.11788	4.71	0.8591	13.44	2.51	49.72	7.61	9.70	16.13	7.12	92.80
carbon dioxide	AA ethyl ester	48	0.13880	0.97	1.1233	23.26	1.17	37.41	1.53	15.16	10.26	0.94	84.76
carbon dioxide	acetone	178	0.06228	3.76	2.1316	13.74	5.05	11.71	4.15	5.64	5.48	20.26	38.16
carbon dioxide	acridine	6	0.08914	2.87	1.2634	16.55	2.85	15.47	3.50	4.93	12.06	10.72	72.93
carbon dioxide	adamantanone	8	0.19714	2.53	1.4379	-2.78	2.59	29.47	31.54	18.17	13.45	9.10	28.25
carbon dioxide	α-linolenic acid	56	0.11547	3.94	0.9745	15.74	2.79	26.31	5.15	14.24	9.32	4.65	81.08
carbon dioxide	allylbenzene	15	0.07426	3.49	1.3060	10.81	3.34	10.60	4.39	5.36	8.42	11.96	62.71
carbon dioxide	aniline	15	-0.05610	3.28	1.1791	8.61	2.46	21.45	25.07	33.34	33.91	51.80	92.40
carbon dioxide	anisole	15	0.04049	2.17	1.4822	13.90	2.97	7.70	3.35	7.33	11.77	20.82	64.09
carbon dioxide	anthracene	22	0.12949	2.33	1.6433	22.35	1.75	20.69	10.72	10.38	2.86	1.72	57.43
carbon dioxide	α-pinene	15	0.09612	3.06	1.7055	21.73	3.83	9.38	4.11	7.00	4.66	4.68	59.39

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	α-tocopherol	82	0.21519	2.85	0.9419	18.16	2.21	64.17	9.43	31.55	5.63	16.48	65.05
carbon dioxide	β-carotene	90	0.17275	2.68	0.6748	16.79	2.26	144.58	8.79	14.88	20.36	5.82	112.10
carbon dioxide	behenic acid ethyl ester	17	0.17179	1.53	1.2263	27.32	0.86	65.88	2.73	21.34	5.03	6.43	78.86
carbon dioxide	benzene	222	0.10391	7.54	1.4921	-1.03	7.59	11.77	10.21	9.14	9.23	13.21	40.08
carbon dioxide	benzoic acid	29	0.07014	5.57	1.8170	21.69	6.34	8.54	6.05	9.27	13.02	21.26	65.32
carbon dioxide	benzyl acetate	15	0.04221	2.21	1.3600	16.99	3.02	9.82	3.24	7.79	17.75	20.20	78.14
carbon dioxide	benzylacetone	15	0.05000	2.71	1.0795	9.68	3.76	12.63	9.19	6.19	17.90	18.07	80.40
carbon dioxide	biphenyl	24	0.12074	4.43	1.3557	13.85	3.39	15.21	8.45	10.13	6.94	6.96	56.82
carbon dioxide	β-pinene	15	0.12276	3.65	1.3716	9.22	4.97	10.14	6.66	11.72	4.07	4.08	51.21
carbon dioxide	bromobenzene	15	0.03365	4.66	1.4373	12.25	4.36	9.08	14.21	7.81	10.55	20.44	61.51
carbon dioxide	butyric acid ethyl ester	16	0.08239	2.80	2.2177	27.36	1.89	3.91	3.54	4.31	2.96	7.13	53.47
carbon dioxide	caffeine	21	0.03195	8.16	0.7164	-17.53	4.87	37.00	6.83	22.62	36.24	37.03	107.91
carbon dioxide	capric acid ethyl ester	16	0.11303	2.43	1.7729	29.09	1.44	10.56	2.88	13.46	3.77	2.46	64.43
carbon dioxide	caprylic acid ethyl ester	16	0.10235	1.82	1.7619	26.83	1.67	7.39	2.45	10.23	4.14	1.73	62.85
carbon dioxide	chlorobenzene	15	0.03049	4.12	1.4476	11.52	3.61	8.91	5.24	8.22	10.29	21.63	60.41
carbon dioxide	chrysene	4	0.16203	1.06	1.8594	27.80	2.61	43.90	13.69	16.16	2.80	5.59	56.60
carbon dioxide	citral	15	0.09956	2.52	1.3860	16.29	4.31	10.55	3.50	8.63	5.29	3.45	63.44
carbon dioxide	cobalt(III) acetylacetonate	38	-0.02178	1.80	1.0715	17.87	2.13	125.95	12.44	11.53	29.97	25.24	104.07
carbon dioxide	copper(II) trifluoroacetylacetonate	12	-0.13615	4.63	1.2764	22.66	5.04	72.60	17.87	37.09	49.65	53.26	125.99
carbon dioxide	cycloheptanone	8	-0.00071	2.80	1.8569	23.71	1.85	8.58	5.33	24.01	26.38	40.45	83.17
carbon dioxide	cyclononanone	8	0.01692	3.02	1.7583	25.46	2.33	10.68	4.12	17.62	25.13	31.85	86.08

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^3 \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	cyclopentanone	8	0.01838	0.99	1.8382	18.40	1.03	13.18	7.64	20.31	19.56	37.55	70.71
carbon dioxide	dibenzo-24-crown-8	28	0.16529	1.65	1.0944	24.24	1.93	99.02	9.04	12.73	13.08	2.71	89.14
carbon dioxide	dibenzyl ether	15	0.05662	2.24	1.0702	14.04	3.22	15.81	5.56	5.32	20.72	17.22	88.51
carbon dioxide	diethyl ether	15	-0.02679	15.41	1.0474	-26.59	4.98	32.29	6.98	11.80	12.38	24.74	59.29
carbon dioxide	diisopropyl ether	15	0.02806	11.52	1.0782	-16.29	7.87	29.92	8.47	7.14	6.46	9.41	52.65
carbon dioxide	diolein	9	0.18338	3.74	0.6769	14.02	1.61	77.97	4.84	23.69	9.91	5.27	95.83
carbon dioxide	D-limonene	15	0.10598	3.69	1.3735	12.04	4.06	10.49	4.03	9.32	4.27	4.20	57.32
carbon dioxide	docosahexaenoic acid (DHA)	63	0.11616	2.51	0.9162	18.60	1.63	58.53	9.19	7.28	19.86	8.29	100.02
carbon dioxide	DHA ethyl ester	65	0.15248	1.60	1.0708	22.09	1.45	48.46	1.67	16.73	9.27	2.00	84.14
carbon dioxide	DHA methyl ester	17	0.15558	1.07	1.2079	25.70	0.92	52.38	2.34	16.76	8.37	2.47	81.78
carbon dioxide	eicosapentaenoic acid (EPA)	55	0.11572	3.17	0.9184	16.15	1.79	46.01	7.35	7.79	17.55	7.30	94.51
carbon dioxide	EPA ethyl ester	48	0.13979	1.18	1.1626	24.23	1.06	36.48	1.55	14.98	10.14	1.02	84.21
carbon dioxide	EPA methyl ester	17	0.14362	1.55	1.2964	27.43	0.49	37.76	1.65	17.37	7.27	3.34	79.62
carbon dioxide	ethanol	24	0.05064	2.97	1.9621	6.43	3.21	12.41	4.48	11.29	5.39	32.94	39.86
carbon dioxide	ethyl acetate	15	-0.00519	18.11	0.8254	-49.61	6.71	36.32	8.62	12.75	13.77	26.10	62.20
carbon dioxide	ethyl benzoate	15	0.04491	3.66	1.8993	27.23	2.94	12.20	4.95	3.88	12.77	13.39	72.14
carbon dioxide	ethylbenzene	15	0.09268	1.54	1.8248	18.85	2.28	9.47	4.72	7.44	3.41	4.76	46.77
carbon dioxide	eugenol	15	0.00224	2.68	1.3885	20.62	3.58	10.54	7.33	17.29	28.35	31.11	94.09
carbon dioxide	ferrocene	98	0.04990	3.06	1.2424	6.91	6.35	21.24	19.48	17.32	20.92	32.42	76.45
carbon dioxide	fluorobenzene	15	0.01155	3.57	1.7808	17.76	4.22	10.40	4.34	11.04	11.16	26.57	59.41
carbon dioxide	γ-linolenic acid	142	0.10814	5.00	0.8364	9.15	2.15	33.37	7.90	7.79	16.90	8.37	92.13

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol{\cdot}cm^{-1}{\cdot}s^{-1}{\cdot}K^{-1/2}}$)	V_D ($\mathrm{cm^3{\cdot}mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	γ-linolenic acid ethyl ester	41	0.04630	6.69	0.8603	6.15	5.10	43.72	9.79	6.92	27.87	19.79	105.41
carbon dioxide	γ-linolenic acid methyl ester	52	0.11534	7.34	0.8588	7.53	7.58	47.11	6.85	13.41	10.20	4.68	82.00
carbon dioxide	hexachlorobenzene	14	0.11598	8.71	0.8331	-12.47	4.18	25.04	25.68	10.99	13.01	12.63	71.35
carbon dioxide	iodobenzene	15	0.02343	3.37	1.2680	11.18	2.72	11.69	16.88	12.21	17.69	26.12	73.53
carbon dioxide	*i*-propylbenzene	15	0.09392	2.45	1.6274	17.00	2.00	10.94	4.82	9.27	4.11	4.28	49.12
carbon dioxide	linalool	15	0.09694	3.44	1.3508	14.09	4.02	11.26	3.52	7.24	5.63	4.13	63.29
carbon dioxide	linoleic acid	71	0.09491	5.68	0.8351	9.74	3.73	30.68	7.14	9.63	15.88	7.28	90.41
carbon dioxide	linoleic acid methyl ester	21	0.12807	2.17	1.0645	19.77	1.66	56.92	2.11	15.74	7.44	3.30	77.97
carbon dioxide	methanol	10	0.05609	3.93	2.1980	1.60	2.14	20.87	6.17	16.79	7.10	46.84	33.18
carbon dioxide	monoolein	11	0.09642	3.33	0.8199	13.88	1.22	24.17	5.13	8.71	18.90	7.31	99.51
carbon dioxide	myristic acid ethyl ester	16	0.13321	2.36	1.4546	27.11	2.14	24.88	3.07	15.97	4.92	3.60	71.66
carbon dioxide	myristoleic acid	42	0.06120	5.82	0.8465	4.77	2.66	25.97	13.91	5.68	22.90	14.76	98.00
carbon dioxide	myristoleic acid methyl ester	79	0.01906	9.00	0.7247	-15.38	10.07	68.29	11.93	10.41	19.80	13.01	94.13
carbon dioxide	*N*-(4methoxybenzylidene)-4-*n*-butylaniline	5	0.19411	1.41	2.1419	29.00	0.33	42.04	30.23	17.85	5.56	7.95	47.09
carbon dioxide	naphthalene	83	0.09961	8.78	1.4146	11.79	8.29	18.59	10.29	10.81	10.77	11.51	56.10
carbon dioxide	*n*-butylbenzene	15	0.08608	1.90	1.4109	15.95	2.97	11.18	2.77	6.29	5.39	5.62	61.07
carbon dioxide	*n*-decane	5	0.24037	3.04	3.8443	36.48	1.47	32.31	27.51	38.51	29.10	31.07	10.62
carbon dioxide	*n*-dodecane	5	0.25131	4.81	4.3507	39.93	2.99	37.54	29.20	40.87	29.79	33.31	11.47
carbon dioxide	*n*-heptane	5	0.18633	2.80	3.9421	35.67	1.00	20.99	19.03	28.91	22.68	20.51	16.50
carbon dioxide	*n*-hexane	5	0.15090	2.58	3.9838	35.55	2.09	16.06	14.11	22.91	18.40	13.51	20.98
carbon dioxide	nitrobenzene	15	0.05167	2.42	1.2975	9.79	3.33	9.96	4.21	8.79	13.98	22.29	67.96

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^3 \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*n*-nonane	5	0.22570	3.06	4.0604	37.02	1.43	29.33	25.69	36.45	27.94	28.90	11.31
carbon dioxide	*n*-octane	5	0.20710	3.16	4.1527	37.05	1.66	25.60	22.91	33.41	25.91	25.59	13.16
carbon dioxide	*n*-pentane	5	0.09826	2.87	4.0586	35.82	1.67	9.12	6.62	13.23	11.26	2.49	28.89
carbon dioxide	*n*-pentylbenzene	31	0.08492	2.20	1.6168	21.86	3.95	12.96	3.96	8.27	5.37	4.32	62.60
carbon dioxide	*n*-propylbenzene	34	0.06420	10.64	0.8647	-17.49	5.03	25.18	8.65	12.75	14.62	15.88	66.76
carbon dioxide	*n*-tetradecane	5	0.25003	6.96	4.3703	41.99	3.32	43.05	25.26	38.78	25.35	30.40	20.42
carbon dioxide	*n*-undecane	5	0.25308	3.79	4.1553	38.28	1.85	35.87	29.69	40.94	30.82	33.61	8.96
carbon dioxide	oleic acid	19	0.09848	5.40	0.8088	9.94	2.14	37.36	7.78	10.03	16.61	7.86	91.81
carbon dioxide	oleic acid ethyl ester	5	0.04134	6.29	0.5458	-23.03	0.97	53.72	5.13	5.72	27.68	16.67	113.19
carbon dioxide	oleic acid methyl ester	19	0.00526	8.22	0.5031	-34.23	1.93	65.15	6.26	6.50	31.10	19.06	117.76
carbon dioxide	palladium(II) acetylacetonate	125	-0.02284	2.56	1.2460	17.11	4.65	91.51	18.95	21.93	32.80	36.33	100.26
carbon dioxide	palmitic acid ethyl ester	17	0.13180	1.38	1.3142	26.47	0.61	30.82	1.46	15.14	8.02	1.75	78.79
carbon dioxide	*p*-dichlorobenzene	13	0.04635	3.63	1.5067	16.27	3.72	8.76	8.46	10.61	16.00	24.31	71.04
carbon dioxide	phenanthrene	19	0.15914	6.09	1.3448	12.04	5.03	23.94	13.72	13.96	7.78	8.06	51.15
carbon dioxide	phenol	109	0.03366	3.09	1.3641	2.62	4.61	8.02	5.21	21.47	18.22	40.23	66.70
carbon dioxide	phenylacetic acid	16	0.07464	1.55	1.7122	22.71	1.80	6.41	1.62	4.25	12.95	16.60	69.79
carbon dioxide	phenylacetylene	15	0.04583	1.59	1.6377	17.26	1.58	7.61	4.46	7.80	12.00	21.03	64.46
carbon dioxide	phenylmethanol	15	0.03313	1.61	1.5257	16.57	2.54	8.05	7.02	13.91	18.50	28.26	73.87
carbon dioxide	pyrene	18	0.12463	2.38	1.5497	23.47	1.84	26.23	6.84	9.18	5.95	2.73	65.38
carbon dioxide	squalene	5	0.14122	4.21	1.9069	36.68	1.87	50.04	10.81	13.56	11.21	3.78	85.24
carbon dioxide	stearic acid ethyl ester	17	0.13988	1.41	1.2474	26.37	1.03	41.53	1.65	16.25	8.48	2.16	81.42

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	styrene	15	0.03001	3.97	1.6454	18.93	4.39	8.35	9.17	5.38	9.91	17.70	62.10
carbon dioxide	*tert*-butylbenzene	15	0.09222	3.10	1.8018	23.59	3.62	9.25	3.26	7.92	3.35	3.51	56.49
carbon dioxide	tetrahydrofuran	15	0.01091	13.12	1.1871	-22.18	4.99	22.16	8.80	15.96	12.43	34.15	58.17
carbon dioxide	thenoyltrifluoroacetone	15	-0.02344	3.19	1.1938	18.09	3.05	13.70	4.04	30.20	41.38	45.60	112.83
carbon dioxide	toluene	35	0.07407	4.01	1.6490	11.46	4.14	8.44	5.43	5.32	5.03	11.33	48.08
carbon dioxide	triarachidonin	27	0.18755	6.00	0.4912	6.85	0.82	149.23	10.98	17.49	20.63	8.39	116.86
carbon dioxide	trierucin	101	0.16378	7.58	0.3731	-2.73	2.95	146.62	7.37	13.57	31.19	14.68	140.57
carbon dioxide	trifluoroacetylacetone	15	0.05745	1.61	1.7229	19.57	2.18	6.36	14.09	3.74	9.06	15.88	61.49
carbon dioxide	trinervonin	38	0.18060	6.61	0.3962	2.77	2.86	163.95	6.58	16.62	27.91	12.12	136.63
carbon dioxide	triolein	10	0.16986	5.73	0.4442	-1.58	1.26	100.27	5.95	11.80	28.90	12.39	131.65
carbon dioxide	ubiquinone CoQ10	80	0.17148	3.43	0.6220	16.09	4.09	141.53	7.87	13.90	23.98	8.60	120.85
carbon dioxide	vanillin	15	0.04536	1.70	1.5345	21.13	2.03	10.92	2.63	12.64	21.65	26.02	82.53
carbon dioxide	vitamin K_1	16	0.23026	3.00	0.8940	16.80	2.22	106.89	9.99	27.19	4.19	11.84	72.64
carbon dioxide	vitamin K_3	20	0.13593	4.59	1.1807	8.84	2.70	24.21	8.88	9.77	7.48	7.14	61.05
chlorotrifluoromethane	acetone	10	-0.11516	4.27	0.9096	19.58	2.56	5.85	8.40	23.27	29.79	23.24	25.58
chlorotrifluoromethane	*p*-xylene	8	-0.15246	8.93	0.4851	-13.32	2.28	38.21	7.10	23.77	22.00	21.70	39.07
ethane	1-octene	6	0.03142	5.28	1.2050	12.75	1.40	11.82	4.02	4.78	50.84	55.22	41.98
ethane	1-tetradecene	9	0.11067	2.05	1.5925	38.24	1.61	18.87	7.84	17.61	37.74	26.61	37.54
sulfur hexafluoride	1,3,5-trimethylbenzene	10	-0.06452	5.00	0.5377	18.96	4.59	14.17	6.88	33.06	45.21	41.60	30.23
sulfur hexafluoride	benzene	9	-0.05035	6.31	0.6679	1.44	10.58	7.33	16.16	39.39	51.09	42.39	39.89
sulfur hexafluoride	benzoic acid	6	-0.12521	1.88	0.6061	40.87	2.61	17.30	13.12	149.89	76.57	103.02	194.96

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
sulfur hexafluoride	carbon tetrachloride	6	-0.09832	4.48	0.6877	35.40	5.18	13.73	21.28	37.99	33.97	31.82	42.27
sulfur hexafluoride	naphthalene	5	-0.00670	7.21	1.1687	67.42	5.52	11.07	9.65	77.19	29.47	40.69	120.66
sulfur hexafluoride	*p*-xylene	52	-0.03190	5.71	0.5781	19.73	12.41	7.75	11.03	23.28	41.80	35.17	21.67
sulfur hexafluoride	toluene	11	-0.04438	6.19	0.5288	-18.56	9.73	7.21	12.93	37.76	51.56	44.06	35.72
					Liquid Systems								
2,2,4-trimethylpentane	1,3,5-trimethylbenzene	4	-0.18230	3.22	1.0142	150.50	0.84	36.05	-	58.70	68.00	105.27	48.48
2,2,4-trimethylpentane	benzene	4	-0.10507	1.26	1.1336	145.53	1.61	26.78	-	48.72	43.89	116.08	3.12
2,2,4-trimethylpentane	ethylbenzene	4	-0.14632	1.27	0.8035	144.09	1.33	35.01	-	55.63	60.58	107.53	39.77
2,2,4-trimethylpentane	*o*-xylene	4	-0.13140	2.33	0.9929	147.66	2.24	29.54	-	51.64	56.09	102.80	35.68
2,2,4-trimethylpentane	*p*-xylene	4	-0.07683	2.81	0.7954	140.69	1.94	17.09	-	35.18	39.81	79.76	21.86
2,2,4-trimethylpentane	toluene	4	-0.09552	1.55	1.0099	144.99	1.58	23.72	-	43.53	43.79	98.76	4.53
cyclohexane	argon	6	-0.19274	4.61	2.6698	96.95	2.44	43.30	-	21.29	36.48	49.69	55.63
cyclohexane	carbon tetrachloride	6	-0.30516	9.86	1.3613	102.47	1.11	76.72	-	6.41	5.52	26.29	10.65
cyclohexane	ethane	5	-0.29956	9.04	2.0214	100.00	2.40	106.17	-	25.57	32.30	17.02	49.22
cyclohexane	ethylene	5	-0.32459	7.98	2.1435	99.75	2.30	102.01	-	25.19	33.48	21.04	50.76
cyclohexane	krypton	6	-0.21552	4.33	2.1405	98.04	1.26	66.64	-	8.49	23.56	63.83	45.49
cyclohexane	methane	6	-0.25714	6.40	2.8585	99.81	0.68	40.39	-	28.46	39.35	24.92	56.38
cyclohexane	phenanthrene	8	-0.13688	18.07	0.9775	101.00	4.31	6.34	-	39.49	30.69	27.25	29.80
cyclohexane	*p*-xylene	8	-0.14215	14.32	1.2210	100.22	3.88	28.73	-	40.98	36.75	24.95	38.43
cyclohexane	tetrabutyltin	7	-0.52376	17.12	0.7438	103.12	2.35	13.61	-	6.48	16.43	12.44	21.90
cyclohexane	tetraethyltin	7	-0.46562	14.93	1.0441	102.93	2.16	57.13	-	5.80	7.45	20.03	6.75

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
cyclohexane	tetramethyltin	7	-0.36392	12.27	1.2553	102.25	1.25	94.10	-	4.80	5.16	40.12	3.53
cyclohexane	tetrapropyltin	6	-0.48181	14.12	0.8573	102.94	2.10	21.82	-	4.89	12.46	14.80	14.08
cyclohexane	toluene	12	-0.35350	18.29	1.3305	100.99	2.85	55.83	-	26.14	24.81	24.36	26.52
cyclohexane	xenon	6	-0.26748	5.63	1.8186	99.39	1.15	85.28	-	5.62	15.35	60.65	37.97
n-decane	12-crown-4	4	-0.12568	3.17	0.5689	183.45	2.87	40.09	-	24.21	27.07	62.14	7.17
n-decane	15-crown-5	4	-0.13989	5.15	0.4514	182.06	5.22	22.23	-	28.12	35.97	59.91	17.23
n-decane	18-crown-6	4	-0.17021	3.10	0.4654	184.73	3.14	4.80	-	28.17	40.23	54.71	23.10
n-decane	argon	3	-0.13151	2.33	1.8070	179.89	0.32	47.60	-	3.65	26.93	115.17	56.51
n-decane	carbon tetrachloride	3	-0.09022	2.95	0.7923	183.18	0.14	71.32	-	17.93	10.97	73.12	24.32
n-decane	dicyclohexano-18-crown-6	4	-0.20064	1.25	0.3810	185.79	1.16	84.24	-	27.03	49.82	43.17	37.56
n-decane	dicyclohexano-24-crown-8	4	-0.22161	1.71	0.3344	185.84	1.71	137.91	-	29.14	57.42	42.19	47.41
n-decane	krypton	3	-0.13060	1.74	1.3923	180.80	0.78	69.75	-	16.32	9.82	139.73	45.21
n-decane	methane	3	-0.21158	1.26	1.8223	181.67	0.03	46.00	-	12.44	31.11	75.42	57.78
n-decane	*s*-trioxane	4	-0.13736	2.00	0.8812	182.90	0.42	50.22	-	25.93	12.59	100.54	25.52
n-decane	tetrabutyltin	4	-0.22885	3.24	0.4353	185.39	2.16	20.57	-	23.40	38.68	45.00	23.71
n-decane	tetraethyltin	3	-0.14314	4.82	0.5949	183.97	1.42	47.46	-	19.59	21.59	57.36	6.30
n-decane	tetramethyltin	4	-0.18046	3.51	0.7287	183.47	1.43	71.35	-	30.51	21.83	93.97	17.31
n-decane	tetrapropyltin	4	-0.19791	3.92	0.4903	184.67	1.55	24.65	-	23.25	32.67	51.39	15.35
n-decane	xenon	4	-0.12199	2.66	1.1823	181.74	0.62	68.96	-	23.29	4.84	132.95	37.54
n-dodecane	1,3,5-trimethylbenzene	4	-0.13037	3.03	0.4609	213.97	0.79	119.21	-	16.71	13.82	52.67	19.88
n-dodecane	acetone	5	-0.16929	1.39	0.8244	215.52	1.68	102.53	-	16.62	3.20	86.12	34.68

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^3 \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-dodecane	benzene	4	-0.14203	1.42	0.6766	214.82	1.30	122.54	-	16.31	5.03	74.30	30.83
n-dodecane	carbon dioxide	9	-0.15144	2.65	1.2167	210.03	2.20	23.83	-	10.06	30.15	93.72	58.09
n-dodecane	carbon monoxide	9	-0.21802	7.33	1.4392	212.70	5.90	27.26	-	17.45	38.00	72.63	62.82
n-dodecane	hydrogen	9	-0.39095	7.86	3.9660	215.14	5.29	47.80	-	59.75	71.88	13.38	83.78
n-dodecane	linoleic acid methyl ester	4	-0.23215	2.08	0.2853	217.39	0.92	41.86	-	13.66	29.88	24.46	18.23
n-dodecane	*m*-xylene	4	-0.09820	2.36	0.5477	214.25	1.54	108.51	-	9.33	5.86	48.13	27.84
n-dodecane	naphthalene	5	-0.06931	2.91	0.5064	214.04	1.41	81.24	-	12.27	8.59	48.57	23.94
n-dodecane	*n*-decane	5	-0.08227	4.61	0.5822	219.24	2.98	29.97	-	21.54	18.92	12.00	30.49
n-dodecane	*n*-hexadecane	5	-0.14672	4.44	0.4466	221.99	6.69	19.30	-	14.84	12.56	12.69	14.84
n-dodecane	*n*-octane	9	-0.08135	2.27	0.6640	218.97	1.48	25.45	-	21.35	21.56	12.11	34.17
n-dodecane	*n*-tetradecane	5	-0.15173	6.03	0.4729	221.14	7.84	17.19	-	18.00	15.58	15.38	19.31
n-dodecane	toluene	4	-0.09938	1.68	0.6374	214.93	2.01	110.79	-	9.90	4.09	55.84	30.91
n-eicosane	carbon dioxide	5	-0.28359	4.12	0.8724	352.03	2.07	21.16	-	16.80	37.40	108.39	64.95
n-eicosane	carbon monoxide	5	-0.36788	4.82	1.0324	354.30	2.43	31.74	-	19.36	44.76	84.64	69.09
n-eicosane	hydrogen	5	-0.63053	6.38	3.0212	357.65	4.65	36.80	-	62.00	76.22	13.99	87.20
n-eicosane	*n*-dodecane	5	-0.16067	4.74	0.3222	361.84	4.28	60.70	-	14.60	18.07	8.99	43.31
n-eicosane	*n*-hexadecane	5	-0.18720	5.13	0.2678	362.04	3.44	55.72	-	13.47	13.51	9.14	26.38
n-eicosane	*n*-octane	5	-0.14837	4.92	0.4003	359.67	4.78	56.15	-	16.80	25.59	12.53	50.47
n-heptane	*n*-decane	5	-0.01037	3.09	0.9631	132.45	1.65	6.81	-	34.06	22.77	18.52	30.40
n-heptane	*n*-dodecane	5	-0.00291	4.65	0.8855	132.67	2.18	15.55	-	30.61	19.05	18.51	23.25
n-heptane	*n*-hexadecane	8	-0.04914	3.77	0.7499	133.82	3.09	24.56	-	33.68	22.78	24.44	24.34

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-heptane	*n*-octane	4	0.00047	3.45	1.1427	133.32	1.92	5.00	-	35.23	26.79	20.30	35.41
n-heptane	*n*-tetradecane	5	-0.01066	4.50	0.8028	133.05	2.96	29.65	-	29.40	18.67	18.71	19.23
n-hexadecane	carbon dioxide	10	-0.27704	3.08	0.9379	278.97	1.91	34.82	-	12.21	33.40	102.80	61.01
n-hexadecane	carbon monoxide	10	-0.37970	5.40	1.0499	280.25	3.08	51.49	-	13.21	38.83	87.01	64.22
n-hexadecane	hydrogen	10	-0.67791	3.00	2.1314	268.40	7.32	37.24	-	55.28	70.82	23.96	83.58
n-hexadecane	*n*-decane	5	-0.18681	3.82	0.4751	291.18	6.01	62.45	-	13.07	14.69	13.91	39.13
n-hexadecane	*n*-dodecane	5	-0.16438	1.38	0.3976	288.61	2.43	55.76	-	14.96	15.22	16.29	24.68
n-hexadecane	*n*-octane	10	-0.16926	3.16	0.5159	289.46	3.65	64.04	-	13.88	18.00	16.54	42.79
n-hexadecane	*n*-tetradecane	5	-0.16297	2.41	0.3774	290.23	5.42	42.01	-	13.59	12.80	14.22	21.72
n-hexane	1,3,5-trimethylbenzene	20	-0.03642	3.51	0.8743	101.17	14.54	5.88	-	48.09	46.23	46.11	47.59
n-hexane	acetone	5	-0.02365	2.62	1.4801	111.01	3.03	7.37	-	5.42	5.90	64.29	25.75
n-hexane	acetonitrile	7	0.04660	15.08	1.1551	102.14	5.93	22.16	-	115.32	110.08	246.91	60.48
n-hexane	benzene	36	-0.02810	11.86	1.1371	103.51	14.54	26.17	-	80.10	82.83	114.18	74.29
n-hexane	carbon disulphide	10	0.08914	25.91	1.1409	102.23	4.66	64.04	-	178.18	168.35	362.18	98.69
n-hexane	indole	4	-0.01577	4.32	0.4384	84.37	2.83	10.84	-	10.40	2.18	19.65	9.11
n-hexane	*m*-xylene	5	-0.02762	2.43	1.3601	115.15	2.00	5.49	-	6.24	11.30	36.87	6.26
n-hexane	naphthalene	20	-0.00039	4.62	0.8828	98.35	15.15	10.14	-	49.57	45.58	44.12	49.47
n-hexane	phenanthrene	15	0.00207	4.58	0.6767	81.65	11.81	12.83	-	63.76	56.82	53.53	60.56
n-hexane	p-xylene	17	-0.00956	5.21	0.9088	93.68	16.35	8.34	-	56.45	54.15	49.43	56.94
n-hexane	toluene	28	-0.00821	12.01	1.0354	102.80	16.17	18.14	-	78.86	82.91	106.45	76.21
n-octacosane	carbon dioxide	5	-0.52119	4.73	0.5620	485.36	2.08	36.43	-	173.15	68.01	524.73	10.33

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ $(\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2})$	V_D $(\text{cm}^3\cdot\text{mol}^{-1})$	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-octacosane	carbon monoxide	5	-0.63474	6.87	0.7097	489.28	3.79	50.03	-	131.14	41.98	430.14	22.17
n-octacosane	hydrogen	5	-0.91913	6.72	1.8034	483.00	2.26	32.37	-	12.28	40.01	175.33	68.36
n-octacosane	*n*-dodecane	5	-0.43090	2.39	0.1909	498.98	3.77	142.06	-	183.91	149.00	231.40	68.82
n-octacosane	*n*-hexadecane	5	-0.44961	1.66	0.1543	499.57	4.40	149.34	-	200.39	175.99	227.40	92.39
n-octacosane	*n*-octane	5	-0.40864	2.73	0.2457	496.79	2.65	123.16	-	166.97	119.42	246.24	43.11
n-octane	1,3,5-trimethylbenzene	4	-0.03237	2.16	0.8117	148.56	0.28	22.30	-	8.13	16.08	43.28	1.08
n-octane	argon	4	-0.07673	3.16	1.9181	142.44	2.94	19.90	-	2.39	20.76	117.57	51.97
n-octane	benzene	4	0.02089	3.60	1.0124	144.89	0.22	16.11	-	0.98	2.07	48.93	32.43
n-octane	carbon tetrachloride	4	-0.02667	3.22	1.0157	148.85	0.59	34.74	-	12.51	11.62	65.23	22.48
n-octane	ethyl benzene	4	-0.02758	4.07	0.7797	145.55	1.55	22.88	-	6.06	10.97	44.99	6.40
n-octane	krypton	4	-0.08222	3.96	1.5181	143.52	2.86	37.40	-	16.13	5.08	135.75	41.27
n-octane	methane	4	-0.11889	1.62	2.0640	145.64	2.95	18.87	-	12.50	27.42	72.82	54.70
n-octane	*o*-xylene	4	0.01904	1.42	1.0323	149.57	0.87	13.46	-	1.66	3.84	36.40	12.53
n-octane	*p*-xylene	4	0.05529	1.60	1.0964	149.51	0.86	6.18	-	8.17	3.69	25.17	18.66
n-octane	tetrabutyltin	4	-0.14964	3.08	0.5544	150.12	1.13	13.75	-	16.40	28.68	29.94	21.47
n-octane	tetraethyltin	5	-0.07103	10.03	0.7116	148.73	6.31	17.69	-	20.42	26.20	53.34	13.76
n-octane	tetramethyltin	4	-0.11523	5.72	0.8621	147.09	1.35	36.01	-	19.45	18.35	76.82	19.03
n-octane	tetrapropyltin	4	-0.12798	4.45	0.6115	149.11	1.10	8.07	-	16.00	24.91	36.66	16.32
n-octane	toluene	4	0.00987	3.78	0.9051	145.10	1.51	15.73	-	1.81	2.10	41.37	28.80
n-octane	xenon	4	-0.07319	3.79	1.3238	145.23	1.84	42.84	-	20.04	5.65	124.07	34.70
propane	1-octene	8	0.00487	1.75	1.5602	57.26	1.91	9.91	-	7.32	27.75	34.70	19.51

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD
propane	1-tetradecene	8	0.05334	1.78	1.3094	58.74	1.92	40.78	-	16.66	25.61	15.79	24.66
Gas Systems													
argon	ethane	9	-0.02405	1.23	4.7507	7729.39	1.72	12.61	-	-	-	-	-
argon	hydrogen	5	0.00898	2.95	23.0413	3938.78	2.29	72.01	-	-	-	-	-
argon	*i*-butane	8	-0.07484	2.46	2.6722	5654.17	1.33	71.90	-	-	-	-	-
argon	methane	9	-0.00946	2.70	7.7281	8889.20	1.49	22.49	-	-	-	-	-
argon	*n*-butane	8	-0.06396	1.79	2.8191	6520.36	1.24	67.17	-	-	-	-	-
argon	neon	25	-0.01116	1.85	10.3605	6724.28	5.46	35.22	-	-	-	-	-
argon	propane	9	-0.03458	0.86	3.6775	7706.29	0.78	38.79	-	-	-	-	-
carbon dioxide	ethylene	48	-0.01413	6.77	2.9026	-3.87	4.79	9.12	-	-	-	-	-
carbon dioxide	hydrogen	7	-0.01758	0.34	19.8027	5898.70	0.28	73.95	-	-	-	-	-
carbon monoxide	helium	7	0.07603	0.22	22.1377	5018.43	0.16	69.03	-	-	-	-	-
carbon monoxide	hydrogen	7	0.01337	0.20	22.1377	5018.43	0.16	70.85	-	-	-	-	-
deuterium	hydrogen	5	0.07457	1.94	34.7676	2840.99	1.14	35.80	-	-	-	-	-
ethane	nitrogen	14	-0.03094	0.99	4.8313	6847.25	0.95	11.79	-	-	-	-	-
ethylene	carbon dioxide	49	0.02316	4.63	3.0975	5.29	3.53	9.95	-	-	-	-	-
ethylene	nitrogen	7	-0.01717	0.53	5.0043	5395.35	0.38	8.64	-	-	-	-	-
helium	hydrogen	17	0.09643	2.94	49.5883	5467.93	5.16	51.24	-	-	-	-	-
krypton	argon	6	0.00316	3.14	5.6514	11563.83	2.91	32.57	-	-	-	-	-
krypton	helium	6	0.05413	1.57	22.0575	9617.38	2.38	81.76	-	-	-	-	-
krypton	neon	17	-0.00475	2.71	9.0618	8120.62	2.92	53.32	-	-	-	-	-

Table 2. (*Continued*)

System			LJ-1 (This Work: Eqs. (16) – (25))		DHB (Eq. (B.15))			Zhu (Eqs. (B.8) – – (B.14))	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Solvent (1)	Solute (2)	NDP	k_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD
krypton	xenon	8	0.00835	2.86	3.3325	13066.53	2.29	9.25	-	-	-	-	-
methane	carbon dioxide	10	-0.00074	1.63	5.9479	6501.16	1.72	19.26	-	-	-	-	-
methane	tetrachloroethene	5	-0.08171	0.24	2.8076	7640.69	0.11	110.69	-	-	-	-	-
neon	deuterium	5	0.04500	2.39	24.0282	3212.22	1.12	46.96	-	-	-	-	-
neon	helium	24	0.06670	1.65	28.0397	2125.92	1.25	57.07	-	-	-	-	-
neon	hydrogen	5	0.05089	1.76	31.7987	2881.11	0.63	61.10	-	-	-	-	-
neon	xenon	6	-0.00315	0.88	6.4366	4241.29	0.78	61.51	-	-	-	-	-
nitrogen	helium	8	0.02676	2.63	21.4938	6427.19	2.11	66.53	-	-	-	-	-
nitrogen	hydrogen	29	0.03686	1.24	23.3826	4968.86	1.25	72.28	-	-	-	-	-
nitrogen	methane	7	0.00762	2.34	7.4175	6561.84	1.81	18.82	-	-	-	-	-
nitrogen	*n*-butane	5	-0.09621	3.38	2.6491	3362.34	0.96	75.74	-	-	-	-	-
nitrogen	propane	6	-0.09232	2.61	3.2798	4492.50	0.74	52.52	-	-	-	-	-
oxygen	helium	8	0.03223	1.43	21.0509	4501.28	1.36	66.70	-	-	-	-	-
oxygen	hydrogen	13	0.04380	1.21	26.2335	6132.89	0.50	72.82	-	-	-	-	-
sulfur hexafluoride	cyclohexane	5	-0.05083	0.48	1.1504	8141.63	0.12	2.50	-	-	-	-	-
sulfur hexafluoride	methylcyclohexane	5	-0.05699	0.85	1.1703	10547.92	0.32	11.66	-	-	-	-	-
tetrafluoromethane	1,1,1-trichloroethane	5	-0.02521	0.93	1.4470	7233.94	0.86	37.93	-	-	-	-	-
tetrafluoromethane	tetrachloroethene	5	-0.06511	2.24	1.0459	3426.96	0.92	51.75	-	-	-	-	-

LJ force constants. (The solute and solvent LJ parameters are estimated as function of T_c and V_c by Eqs. (21); whenever unknown, they may be estimated by appropriated models, as those identified in the notes of Table 3 in the original paper). Hence, the prediction of $D_{12,\mathrm{Real}}$ is accomplished explicitly: $D_{12,\mathrm{Real}} = D_{12,\mathrm{Real}}\left(T, \rho_1; M_1, M_2, \sigma_{\mathrm{LJ},1}, \sigma_{\mathrm{LJ},2}, \varepsilon_{1,\mathrm{LJ}}, \varepsilon_{2,\mathrm{LJ}}, k_{12}\right)$. This work provides k_{12}'s for 309 systems in Table 2, but for distinct systems it is possible to firstly optimize k_{12} whenever a few data points are available. It is worth noting that the optimization is very simple to carry out, since Eq. (16) is linear in $\left(1-k_{12}\right)^{-2}$.

(2) The calculation results in Table 3 show that the LJ-1 equation behaves equally well for gases (AARD = 2.63%), liquids (AARD = 6.22%), and SCFs (AARD = 4.12%), giving rise to a grand AARD of only 4.26%. Such results prove that one binary parameter seems sufficient for good representation of tracer diffusivities of all the systems studied, which makes LJ-1 a confident correlation.

(3) It is remarkable the good performance achieved for systems completely unknown, in light of the fact that their LJ parameters were calculated from critical constants also estimated: *e.g.*, systems containing 1,1'-dimethylferrocene, cobalt(III) acetylacetonate, copper(II) trifluoroacetylacetonate, ferrocene, palladium(II) acetylacetonate, tetraethyltin, tetramethyltin, tetrapropyltin and tetrabutyltin. In these cases, the unique properties already known were the molecular weight and normal boiling point. It is worth noting that most group contribution methods available to estimate T_c, P_c and V_c do not comprehend metallic atoms like Co, Cu, Fe, Pd, Sn, etc. Hence, the critical constants have been calculated by Klincewicz method [1, 29]. Even so, the average AARDs found for each systems were surprisingly good, 3.90%.

(4) Figure 4 shows that the calculated diffusivities plotted against the experimental ones concentrate along the diagonals for the three physical states. Such systematic behaviour, along with the low AARDs found, assures the consistency and the statistically desirable behaviour of our model. Three distinct graphics were presented due to the very different orders of magnitudes of the diffusivities for gases, liquids and supercritical fluids.

(5) From Table 2 it may be observed that the absolute values of k_{12} are lower for

Table 3. Relative deviations for the supercritical, liquid and gas systems.

System	NDP	NS	LJ-1 (This Work: Eqs. (16) – (25))	DHB (Eq. (B.15))	Zhu (Eqs. (B.8) – – (B.14)	HYS (Eqs. (B.6) and (B.7))	WC (Eq. (B.1))	TC (Eqs. (B.2) and (B.3))	Sch (Eq. (B.4))	RD (Eq. (B.5))
Supercritical	4278	171	4.12	3.78	37.26	8.78	13.86	15.88	17.37	73.85
Liquid	641	101	6.22	5.30	39.03	—	39.74	40.86	73.67	42.68
Gas	422	37	2.63	2.33	39.95	—	—	—	—	—
Total	5341	309	4.26	3.85	37.68	8.78	17.23	19.14	24.71	69.79

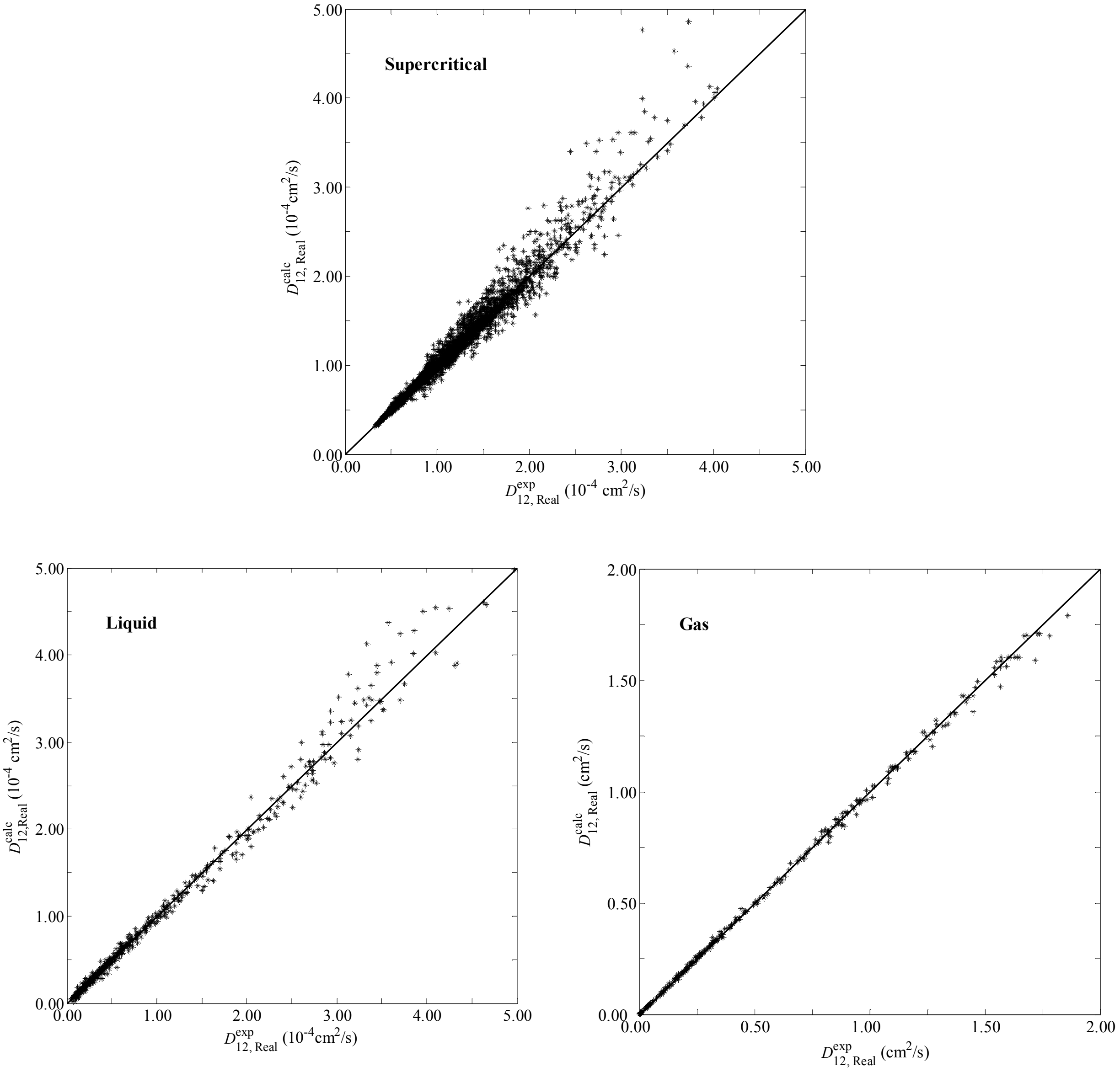

Figure 4. Comparison between calculated and experimental tracer diffusivities for supercritical, liquid and gas systems.

gases than for liquids and supercritical fluids. Furthermore, k_{12} is frequently negative for liquids and generally positive for supercritical systems, which implies that such corrections tend to decrease the starting values provided by $D_{12,\mathrm{LJ}}$ (Eq. (16)) for liquids, and to increase their estimates for supercritical fluids. Such results could be taken as a guideline when k_{12} or experimental data are not available. For these cases, one may propose the following first guesses: $k_{12} = 0.08$ for supercritical, $k_{12} = -0.17$ for liquids, and $k_{12} = 0.00$ for gaseous systems.

(6) It is important to emphasize that many experimental points of our D_{12} database lie outside the validity range of our F_{12} HS correction factor (Eq. (23)), particularly the size ratio $\sigma_2/\sigma_1 = 0.25 - 1.00$. Notwithstanding the solutes diameters are frequently higher than those of the solvents (see Table 3 in the original paper), our model provides very good results globally. Another advantage of the model is that it is also able to represent systems containing polar compounds like alcohols, although it was derived on the basis of the LJ model.

(7) With respect to the models adopted for comparison, Table 3 points out that the hydrodynamic equations of Tyn-Calus [1, 24], Scheibel [1, 3, 25] and Reddy-Doraiswy [1, 3, 26] performs deficiently with AARDs between 19.14 and 69.79 %; the Wilke-Chang [1, 3, 23] equation offers interesting results, if one takes into account it has no parameters and furnishes $\mathrm{AARD_{WC}} = 17.23\%$. The predictive He-Yu-Su model [27] has been only utilized for supercritical solvents, because it was designed for them, giving rise to $\mathrm{AARD_{HYS}} = 8.78\%$. The Zhu *et al.* [6] expression performs more poorly, as its average absolute relative deviation demonstrates ($\mathrm{AARD_{Zhu}} = 37.68\%$). Despite of possessing two parameters, the Dymond equation [2, 9, 28] exhibits results comparable to those of our one-parameter correlation, $\mathrm{AARD_{DHB}} = 3.85\%$ and $\mathrm{AARD_{LJ\text{-}1}} = 4.26\%$. Besides, this reference equation has presented two physically meaningless results: quite different minimum diffusive free volumes (V_D) for the same solvent, which is not correct, and even negative values (please see Table 2) [4, 9]. Moreover, the DHB equation should be used only for interpolation, which limits its application outside the fitting interval.

4.PII.5. Conclusions

In this work, a new correlation is proposed for the tracer diffusivity of hard spheres, more specifically the correction factor F_{12} given by Eq. (23), and Eqs. (24) and (25). This F_{12} provides a very good representation of MD data taken from literature (AARD = 4.44%), whereas the well known expressions of Sung and Stell [16], Sun and Chen [19], Easteal and Woolf [18], and Eaton and Akgerman [17] reach 63.89, 24.46, 18.20 and 67.78 %. With this F_{12} factor it was possible to develop a new model for tracer diffusion coefficients of real fluids (LJ-1): Eq. (16) and subsidiary Eqs. (2) and (17) – (25). The proposed LJ-1 model involves only one parameter (k_{12}) and requires the temperature, solvent density, and solute and solvent molecular weight and LJ force constants (these are estimated as function of T_c and V_c). Results calculated for 309 systems and 5341 data points evidence the excellent performance of our correlation, for which AARD = 4.26%. Moreover it is important to emphasize that the new model interprets equally well the diffusive phenomena of gases, liquids and SCFs.

Appendix A

4.PII.A. Expressions for the HS Correction Factor, F_{12}

This appendix summarizes the hard sphere correction factors adopted for comparison with the new model proposed in this work (Eq. (23)), namely: Sung and Stell [16], Eaton and Akgerman [17], Easteal and Woolf [18], and Sun and Chen [19]. The Sung and Stell [16] expression was derived from first principles at solvent-solute microscale level, and can be considered an improvement of the Enskog model at low densities and simultaneously fulfils the correct hydrodynamic limit enclosed in the Stokes-Einstein law at high density limit. It is an analytic expression requiring viscosity. The Sung and Stell [16] equation has theoretical fundament, but does not satisfy the restriction imposed by Eq. (12). The development of the expression of Eaton and Akgerman [17] is based on the smooth-hard sphere model theory and molecular dynamics data from Easteal and Woolf [18]. These authors also published an empirical expression for F_{12} [18] (Eq. (A.10)), whose dependence on the size and mass ratios is logarithmic as in our case. The correlation by Sun and Chen [19] is given by Eq. (A.12), which behaves well at higher reduced number densities of solvent, but fails the low density restriction imposed by Eq. (10).

4.PII.A.1. Sung and Stell [16]

Sung and Stell [16] derived analytically an expression which embodies the correct hydrodynamic limit (Stokes-Einstein behaviour) and the Enskog theory:

$$F_{12} = \left(\frac{1+\gamma_B \dfrac{\sigma_1}{\sigma_2}}{1+\gamma \dfrac{\sigma_1}{\sigma_2}} \right)^2 \frac{g(\sigma_{12})}{1+4\varphi_1 g(\sigma_{11})} + \frac{1+\dfrac{\sigma_1}{\sigma_2}}{1+\gamma\dfrac{\sigma_1}{\sigma_2}} \frac{D_{12,\mathrm{H}}}{D_{12,\mathrm{E}}} \tag{A.1}$$

where γ and γ_B $\left(\gamma_B \equiv \lim\limits_{\rho_1 \to 0} \gamma \right)$ are given by:

$$\frac{1}{\left(1-\gamma^3\varphi_1\right)^3} \left(1-\gamma^3\varphi_1 + \frac{2\gamma^3\varphi_1}{1+\sigma_1/\sigma_2} \right) \left(1-\gamma^3\varphi_1 + \frac{\gamma^3\varphi_1}{1+\sigma_1/\sigma_2} \right) = 1+4\varphi_1 \frac{1-\varphi_1/2}{\left(1-\varphi_1\right)^3} \tag{A.2}$$

The first term in the right hand side of Eq. (A.1) is the Enskog limit, while the second is the hydrodynamic limit; the ratio $D_{12,\mathrm{H}}/D_{12,\mathrm{E}}$ is given by (Sun and Chen [30]):

$$\frac{D_{12,\mathrm{H}}}{D_{12,\mathrm{E}}}=2.881\left(1+\frac{\sigma_2}{\sigma_1}\right)\left(1+\frac{m_1}{m_2}\right)^{-1/2}\frac{\varphi_1\,g(\sigma_{12})}{\eta_{1,\mathrm{HS}}/\eta_1^0} \tag{A.3}$$

where $\eta_{1,\mathrm{HS}}/\eta_1^0$ is the ratio between the viscosities of the HS solvent and ideal gas. Taking into account Enskog formula [2, 9], it is possible to write:

$$\frac{\eta_{1,\mathrm{HS}}}{\eta_1^0}=\left(\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}\right)\times\left(\frac{\eta_{1,\mathrm{E}}}{\eta_1^0}\right)=\left(\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}\right)\left[\frac{1}{g(\sigma_{11})}+3.2\varphi_1+12.180.761\varphi_1^2 g(\sigma_{11})\right] \tag{A.4}$$

Using the MD simulations of Alder *et al.* [31] for the HS fluid, Liu and Ruckenstein [5] proposed the following accurate expression:

$$\frac{\eta_{1,\mathrm{HS}}}{\eta_{1,\mathrm{E}}}=1+0.007825\,\rho_1^{*0.1}\exp\left(6.0037\rho_1^{*3}\right) \tag{A.5}$$

4.PII.A.2. ***Eaton and Akgerman*** [17]

These authors proposed an alternative expression for the correction factor of the HS tracer diffusivity, based on the MD simulations of Easteal and Woolf [18] at different m_2/m_1, σ_2/σ_1, and $V_1/V_{1,0}$ values: m_2/m_1 in the range 0.6 – 10, σ_2/σ_1 in the range 1.0 – 2.0, and $V_1/V_{1,0}$ in the range 1.5 – 2.0. Their model is:

$$F_{12}=a'\frac{V_{0,1}}{V_1}\left[\left(\frac{V_1}{V_{0,1}}\right)^{\alpha}-b_{12}\right]g(\sigma_{12}) \tag{A.6}$$

where

$$\alpha=\frac{\sigma_1}{\sigma_2}-\frac{1}{3} \tag{A.7}$$

$$b_{12}=\left(\frac{m_1}{m_2}\right)^{0.03587}\left[0.6001+0.8491\left(\frac{\sigma_1}{\sigma_2}\right)-0.244\left(\frac{\sigma_1}{\sigma_2}\right)^2\right] \tag{A.8}$$

a' is a function of the molecular size ratio σ_2/σ_1, and $g(\sigma_{12})$ can be calculated according to Mansoori *et al.* [11] (see Eq. (5)), and $V_{0,1}/V_1 = \rho_1^*/\sqrt{2}$. Eq. (A.7) was previously determined by Akgerman *et al.* [32] . Using the same MD simulations, Liu and Ruckenstein [5] obtained:

$$a' = 1.689\,(\sigma_2/\sigma_1)^{2.0674} \tag{A.9}$$

4.PII.A.3. ***Easteal and Woolf*** [18]

Based on MD simulations for tracer diffusion coefficients of HS systems, Easteal and Woolf proposed an empirical model for the molecular-weight ratio (m_2/m_1) dependence of F_{12}/F_{11} involving three coefficients (a_0, a_1 and a_2). Later, Salim and Trebble [33] published the coefficients of the model in terms of ρ_1^* and σ_2/σ_1 :

$$\ln\left(\frac{F_{12}}{F_{11}} \times g^{-1}(\sigma_{12})\right) = a_0 + a_1 \ln\left(\frac{m_2}{m_1}\right) + a_2 \ln^2\left(\frac{m_2}{m_1}\right) \tag{A.10}$$

$$a_0 = -1.02564\,\rho_1^{*4} \ln\left(\frac{\sigma_2}{\sigma_1}\right)$$

$$a_1 = -0.24107 + 1.27589\,h_{12} - 1.35439\,h_{12}^2 + 0.62393\,h_{12}^3 \tag{A.11}$$

$$a_2 = -0.056$$

where: $h_{12} = \rho_1^{*2}(\sigma_2/\sigma_1)$, and $g(\sigma_{12})$ may be calculated according to Mansoori *et al.* [11] (see Eq. (5)).

4.PII.A.4. ***Sun and Chen*** [19]

The F_{12} expression of Sun and Chen has been derived on the basis of the MD simulations of Herman and Alder [22] and Alder *et al.* [12], which cover the following ranges: $0.5 < \sigma_2/\sigma_1 < 1.6$, $0.5 < m_2/m_1 < 4.0$, and $1.5 < V_1/V_{0,1} < 3.0$. Once more, $g(\sigma_{12})$ may be calculated by Eq. (5).

$$F_{12} = 1.0514 \frac{\sigma_{12}^2}{\sigma_1\,\sigma_2}\left(\frac{2}{1+m_1/m_2}\right)^{1/2} \mathrm{g}(\sigma_{12})\left(\frac{m_1}{m_2}\right)^{0.167}\left[1 - 0.9779\rho_1^*\left(\frac{m_1}{m_2}\right)^{0.0165}\left(\frac{\sigma_2}{\sigma_1}\right)^{0.129}\right] \tag{A.12}$$

Appendix B

4.PII.B. Tracer Diffusion Models for Real Systems

This appendix contains the set of D_{12} equations used for comparison in this work. Here we include the classical predictive hydrodynamic models of Wilke and Chang [1, 3, 23], Tyn-Calus [1, 24], Scheibel [1, 3, 25], and Reddy and Doraiswamy [1, 3, 26], whose parameters have been originally correlated and may be taken as universal values for all systems. The predictive He-Yu-Su correlation [27] is specific for supercritical systems and once more their parameters are universal. The 2-parameter equation of Dymond [2, 9, 28] is also studied since it may be taken as the benchmark model with who all molecular models should be compared. Finally, the predictive model of Zhu *et al*. [6] developed for gas, liquid and supercritical systems is also included, and may be taken as the most similar theoretical approach to our model.

4.PII.B.1. Wilke-Chang Equation [1, 3, 23]

$$D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right)=7.4\times10^{-8}\,\frac{T\sqrt{\phi_1\,M_1}}{\eta_1\,V_{\mathrm{bp},2}^{0.6}} \tag{B.1}$$

where ϕ_1 is a dimensionless association factor of the solvent, (for CO$_2$, $\phi_1=1$), η_1 is the solvent viscosity (cP); M_1 is solvent molecular weight ($\mathrm{g\cdot mol^{-1}}$); $V_{\mathrm{bp},2}$ is solute molar volume at its normal boiling point ($\mathrm{cm^3\cdot mol^{-1}}$).

4.PII.B.2. Tyn-Calus Equation [1, 24]

$$D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\left(\frac{V_{\mathrm{bp},2}}{V_{\mathrm{bp},1}^{2}}\right)^{1/6}\left(\frac{\mathbf{P}_1}{\mathbf{P}_2}\right)^{0.6}\frac{T}{\eta_1} \tag{B.2}$$

P identifies parachors, which are related to the liquid surface tension and may be estimated by additive group contributions. For most organic solvents, the approximation may be used:

$$D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\,\frac{V_{\mathrm{bp},1}^{0.267}}{V_{\mathrm{bp},2}^{0.433}}\,\frac{T}{\eta_1} \tag{B.3}$$

4.PII.B.3. ***Scheibel equation*** [1, 3, 25]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{8.2\times10^{-8}T}{\eta_1 V_{\mathrm{bp},2}^{1/3}}\left[1+\left(\frac{3V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)^{2/3}\right] \tag{B.4}$$

4.PII.B.4. ***Reddy-Doraiswamy equation*** [1, 3, 26]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\beta\times\frac{T\sqrt{M_1}}{\eta_1\left(V_{\mathrm{bp},1}\,V_{\mathrm{bp},2}\right)^{1/3}} \tag{B.5}$$

$$\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\leq 1.5\;\Rightarrow\;\beta=10\times10^{-8}$$

$$\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}>1.5\;\Rightarrow\;\beta=8.5\times10^{-8}$$

4.PII.B.5. ***He-Yu-Su correlation*** [27]

$$\begin{gathered}D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=A\times10^{-7}\left(V_1^k-B'\right)T\big/\sqrt{M_2}\\[1ex] k=1,\quad \rho_{\mathrm{r},1}\geq 1.2\\ k=1+\left(\rho_{\mathrm{r},1}-1.2\right)\big/\sqrt{M_1},\quad \rho_{\mathrm{r},1}<1.2\end{gathered} \tag{B.6}$$

The authors found that parameters A' and B' are only approximately dependent on the properties of the solvent:

$$\begin{gathered}A'=0.29263+1.6736\times\exp\left(-\frac{0.75832\sqrt{M_1 V_{\mathrm{c},1}}}{P_{\mathrm{c},1}}\right),\quad \rho_{\mathrm{r},1}\geq 0.21\\[1ex] B'=0.077\,T_{\mathrm{c},1},\quad \rho_{\mathrm{r},1}\geq 0.21\end{gathered} \tag{B.7}$$

4.PII.B.6. Model of Zhu et al. [6]

$$D_{12} = \frac{3}{8\sqrt{\pi}} \sqrt{\frac{\sigma_{12,\mathrm{LJ}}^{2}\ \varepsilon_{12,\mathrm{LJ}}}{m_1}}\ \frac{\sqrt{T_{12}^{*}}}{\rho_{12}^{*}} \left(1 - \frac{\rho_{12}^{*}}{1.029079\, T_{12}^{*\,0.165377}}\right)$$
$$\times \left[1 + \rho_{12}^{*\,0.126978} \left(\frac{0.596103\left(\rho_{12}^{*}-1\right)}{0.539292\left(\rho_{12}^{*}-1\right) + T_{12}^{*\left(0.400152-0.41054\rho_{12}^{*}\right)}} + 0.68856\right)\right] \qquad \text{(B.8)}$$
$$\times \exp\left(-\frac{\rho_{12}^{*}}{2\,T_{12}^{*}}\right)$$

Here, T_{12}^{*} is calculated as before, but distinct reduced density is introduced, as $\sigma_{12,\mathrm{LJ}}$ is implied instead of $\sigma_{2,\mathrm{LJ}}$:

$$T_{12}^{*} = \frac{T}{\varepsilon_{12,\mathrm{LJ}}/k_{\mathrm{B}}} \quad , \qquad \rho_{12}^{*} = \rho_1\, \sigma_{12,\mathrm{LJ}}^{3} \qquad \text{(B.9)}$$

The combining rules adopted to determine binary parameters are:

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_{\mathrm{B}}} = \sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}\right)\times\left(\varepsilon_{2,\mathrm{LJ}}/k_{\mathrm{B}}\right)}$$
$$\text{(B.10)}$$
$$\sigma_{12,\mathrm{LJ}} = \left(1 - k_{12}^{\mathrm{d}}\right)\frac{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}{2} \quad , \qquad \text{where } k_{12}^{\mathrm{d}} = 0.7926\,\frac{\sigma_{2,\mathrm{LJ}} - \sigma_{1,\mathrm{LJ}}}{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}$$

The LJ parameters for the solvent and solute are estimated by distinct expressions:

$$\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}\,(\mathrm{K}) = \frac{T_{\mathrm{c},1}}{T_{\mathrm{c},1}^{*}}\left[1 + 0.47527332\rho_{\mathrm{r},1} + \left(0.06300484 + 0.12374707\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \qquad \text{(B.11)}$$

$$\sigma_{1,\mathrm{LJ}}(\mathrm{cm}) = \left(\frac{\rho_{\mathrm{c},1}^{*}}{\rho_{\mathrm{c},1}}\right)^{1/3}\left[1 - 0.0368868\,\rho_{\mathrm{r},1} + \left(0.00006945 + 0.01089228\,\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \qquad \text{(B.12)}$$

$$\frac{\varepsilon_{2,\mathrm{LJ}}}{k_{\mathrm{B}}} = \frac{T_{\mathrm{c},2}}{1.313} \qquad \text{(B.13)}$$

$$\sigma_{2,\mathrm{LJ}} = \sqrt[3]{\frac{0.13\,\varepsilon_{2,\mathrm{LJ}}}{P_{\mathrm{c},2}}} \qquad \text{(B.14)}$$

Such equations are based on the principle of corresponding states, and on the critical point computed by Johnson *et al.* [34] for the LJ fluid ($P_c^* = 0.13$, $T_c^* = 1.313$, $\rho_c^* = 0.31$).

4.PII.B.7. ***Dymond Free-Volume expression*** [2, 9, 28]

This model embodies two adjustable parameters: B is a constant characteristic of the solvent-solute pair and V_D is a constant related primarily with the solvent.

$$D_{12} = B\sqrt{T}\left(V_1 - V_D\right) \tag{B.15}$$

Nomenclature

AARD	Average absolute relative deviation, $\mathrm{AARD}=\frac{100}{\mathrm{NDP}}\sum_{i=1}^{\mathrm{NDP}}\left|\left(D_{12,\mathrm{Real}}^{\mathrm{cacl}}-D_{12,\mathrm{Real}}^{\mathrm{exp}}\right)/D_{12,\mathrm{Real}}^{\mathrm{exp}}\right|_i$, %
B	Parameter in Eq. (B.15)
D	Tracer diffusion coefficient, $\mathrm{cm}^2\cdot\mathrm{s}^{-1}$
F	Correction factor of HS system
$g(\sigma)$	Radial distribution function at contact
HS	Hard sphere
k_B	Boltzmann constant, $1.380658\times10^{-16}\,\mathrm{g}\cdot\mathrm{cm}^2\cdot\mathrm{s}^{-2}\cdot\mathrm{K}^{-1}$
k_{12}	Binary interaction parameter
LJ	Lennard-Jones
m	Mass of a molecule, g
M	Molecular weight, $\mathrm{g}\cdot\mathrm{mol}^{-1}$
MD	Molecular dynamics
NDP	Number of data points
NS	Number of systems
N_a	Avogadro constant, $6.0221367\times10^{23}\ \mathrm{mol}^{-1}$
P	Pressure, bar
$\mathbf{P}$	Parachors
T	Temperature, K
V	Molar volume, $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$
V_D	Parameter in Eq. (B.15), $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$

Greek letters

η	Viscosity, cP
ζ	Friction coefficient
φ_1	HS packing fraction of solvent
ρ	Number density, N_a/V, cm^{-3}
ε/k_B	Lennard-Jones energy parameter, K
σ	Molecular diameter, cm

Subscripts

bp	Boiling point
BAH	Ben-Amotz and Herschbach
c	Critical property
eff	Effective hard sphere diameter (EHSD)
E	Enskog
HS	Hard sphere fluid
LJ	Lennard-Jones fluid
r	Reduced property
R	Repulsive contribution
Real	Real system
S	Soft attractive contribution
1, 11	Solvent
2	Solute
12	Binary property

Superscripts

0	Ideal gas
*	Reduced quantity

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Paper III

Adapted from

New Tracer Diffusion Correlation for Real Systems Over Wide Ranges of Temperature and Density

Chemical Engineering Journal, **2011**, 166, 49–72.

Abstract

In this work a new model for tracer diffusivities (D_{12}) of real systems is proposed. It is applicable for gases, liquids and supercritical fluids over wide ranges of temperature and density. It was derived on the basis of a very accurate hard sphere expression, following a systematic derivation whereby the softness of repulsive interactions and the contribution of attractive forces were taken into account by means of effective diameters and by coupling an attractive exponential term. The model is explicit and requires only temperature, density, and one diffusive parameter. The validation was accomplished with the largest database ever compiled – 314 binary systems and 5421 data points – giving rise to an average deviation of only 4.40%. Finally it must be emphasized the reliable estimation capability of the new model, *i.e.* its capacity to predict D_{12} at temperatures and densities far away from the conditions of the experimental data utilized to fit its parameter.

4.PIII.1. Introduction

Diffusion is a microscopic level phenomenon that results from particles motion and interaction. The proportionality constant between particles flux and concentration gradient defines the diffusion coefficient [1-2], which may be experimentally measured or estimated by computer simulations or macroscopic models. Typically, tracer diffusion coefficients (D_{12}) are measured by the chromatographic-peak-broadening technique, based on the Taylor-Aris dispersion phenomenon, or by the geometric method [3-4]. With relation to computer simulations, diffusion coefficients, as well as other transport coefficients, may be calculated from equilibrium correlation functions, by observing Green-Kubo formulas or the associated Einstein relations, or going back to first principles and conducting suitable non-equilibrium simulations [2, 5].

The tracer diffusion coefficients are fundamental properties in research and industry. The lack of experimental data and reliable/accurate equations to estimate them in compressed and condensed phases constitute basic shortcomings. For most concentrated liquid mixtures, binary and effective diffusivities can be estimated on the basis of the tracer coefficients of the implied components using the Darken [6], the Vignes [7], or any other of the equations reviewed by Pertler *et al.* [8].

Up till now it is not yet possible to give a rigorous theoretical interpretation of the transport properties of dense fluids, because of the many-body interactions involved and the pair potential energy functions are only known for simple molecules. However, the repulsive interaction in condensed phases plays a major role in their properties, which means that an accurate model for hard spheres (HS) can be used as a first approximation for the major excluded volume and packing effects of real substances. In fact, it has been found that for the liquid viscosity and diffusivity the contribution of the hard sphere term is up to about 70% [2], which evidences its predominance over the attractive contribution. Nonetheless, for proper application of the Hard Sphere (HS) theory, it is necessary to take into account corrections for correlated motions dominant at intermediate and high densities, which may be assessed by computer simulations, specifically by equilibrium and/or non-equilibrium molecular dynamics [1-2, 9].

The main theories for transport properties of dense fluids are the milestone Enskog theory of the HS fluid, the modified Enskog theory applicable to real fluids, the effective hard sphere diameter method, the free-volume approaches (*e.g.*, Dymond, Cohen-Turnbull, Macedo-Litovitz, Chung), the van der Waals and rough hard sphere theories, the hydrodynamic theories based on the Stokes-Einstein equation, the Eyring activated-state theory, and the excess entropy scaling laws which are receiving much attention recently [1-2, 10-21].

In this work it is presented a new tracer diffusion coefficients model for real systems derived on the basis of the HS model fluid. The softness of repulsive interactions is taken into account by means of the effective hard sphere diameter method, and the contribution of attractive forces is considered by combining an Arrhenius exponential term. Such approaches are well grounded in theory [2, 12, 22-23].

The paper is organized as follows: the new tracer diffusion model is derived in Section 4.PIII.2; the equations adopted for comparison are presented in Section 4.PIII.3; the compiled D_{12} database and all data necessary for the calculations are given in Chapter 3; the calculated results and discussion constitute Section 4.PIII.5; in the final section, most important conclusions are drawn.

4.PIII.2. New Tracer Diffusivity Model for Real Systems, $D_{12,\mathrm{Real}}$

The theoretical path adopted in this essay to develop the new tracer diffusion coefficients model for real systems may be summarized as follows: *i*) first, an accurate expression for the tracer diffusivity of the HS fluid ($D_{12,\mathrm{HS}}$) will be adopted; *ii*) then, the effective hard sphere diameter (EHSD) method will be used to take into account essentially the softness of the repulsive potential; *iii*) the effect of the attractive forces, which play an important role especially at low temperatures, will be included by coupling an exponential energetic term with one parameter, α_{12}. The equation so obtained involves three parameters: α_{12} and the LJ force constants σ_{LJ} and $\varepsilon_{\mathrm{LJ}}/k_{\mathrm{B}}$; *iv*) The final model will be than applied to real substances by computing σ_{LJ} and $\varepsilon_{\mathrm{LJ}}/k_{\mathrm{B}}$ with generalized correlations, and fitting the remaining parameter to experimental data available in the literature. In the following, the new $D_{12,\mathrm{Real}}$ model will be derived according to these steps.

The diffusion coefficient of an infinitely diluted gas, D_{12}^0, may be calculated by the rigorous kinetic theory of gases:

$$\rho_1^0 D_{12}^0 = \frac{3}{8\sigma_{12}^2}\left(\frac{k_{\mathrm{B}}T}{2\pi m_{12}}\right)^{1/2} \tag{1}$$

where scripts "0", "1" and "2" denote ideal gas, solvent and solute, respectively, ρ_1 is number density, k_{B} is Boltzmann constant, T is absolute temperature, m_{12} is the reduced mass of the system, and σ_{12} is the distance between the centers of the molecules at collision. The values of m_{12} and σ_{12} are calculated in terms of the individual molecular masses and diameters by:

$$\sigma_{12,\mathrm{LJ}} = \frac{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}{2} \tag{2}$$

$$m_{12} = \frac{m_1 m_2}{m_1 + m_2} = \frac{1}{N_{\mathrm{a}}}\frac{M_1 M_2}{M_1 + M_2} \tag{3}$$

Equation (1) is not applicable to dense gases and liquids since it is based upon the Boltzmann equation for the distribution function. Enskog [1-2, 24] corrected the ideal gas behaviour by taking into account excluded molecular volume effects, which are increasingly important as density raises, and by modifying the collision frequency in the fluid by the unlike pair radial distribution function at contact, $g(\sigma_{12})$. Accordingly, the Enskog equation for the tracer diffusion coefficient is:

$$\frac{\rho_1 D_{12,\mathrm{E}}}{\rho_1^0 D_{12}^0} = \frac{1}{g(\sigma_{12})} \tag{4}$$

In this paper $g(\sigma_{12})$ is calculated by the expression of Mansoori *et al.* [25], due to its simplicity and accuracy. It depends on the solvent HS packing fraction of the solvent, φ_1, and solute solvent diameter ratio:

$$g(\sigma_{12}) = \frac{1}{(1-\varphi_1)^3}\left(1-\varphi_1+\frac{2\varphi_1}{1+\sigma_1/\sigma_2}\right)\left(1-\varphi_1+\frac{\varphi_1}{1+\sigma_1/\sigma_2}\right) \tag{5}$$

For N_1 spheres occupying a volume V, φ_1 is given by:

$$\varphi_1 = \frac{N_1 \pi \sigma_1^3}{6V} = \frac{\pi}{6}\rho_1 \sigma_1^3 = \frac{\pi}{6}\rho_1^* \ , \qquad \rho_1^* \equiv \rho_1 \sigma_1^3 \tag{6}$$

where ρ_1^* is the reduced number density of solvent.

The Enskog theory is not applicable over large density range since it does not take into account the correlated motions between core collisions responsible for backscattering and vortex flow effects. Hence, the HS tracer diffusivity is usually obtained by correcting Enskog theory with a correction factor (F_{12}) dependent upon the reduced density of the solvent, and on the size and mass ratios:

$$D_{12,\mathrm{HS}} = D_{12,\mathrm{E}} \times \left(\frac{D_{12,\mathrm{HS}}}{D_{12,\mathrm{E}}}\right) = D_{12,\mathrm{E}} \times F_{12}\left(\rho_1^*, \sigma_2/\sigma_1, m_2/m_1\right) \tag{7}$$

The F_{12} correlation of Magalhães *et al.* [26] has been adopted in this essay, since it is simple, explicit and very accurate, in comparison to several well known models from literature as those by Sung and Stell [27], Sun and Chen [28], Easteal and Woolf [29], and Eaton and Akgerman [30]. It is applicable in the range $0.4714 \le \rho_1^* \le 0.9428$, $0.25 \le \sigma_2/\sigma_1 \le 1.00$, $0.01 \le m_2/m_1 \le 4.00$:

$$F_{12} = \frac{F_{11} + \rho_1^{*1.7}\left[a\ln(\sigma_2/\sigma_1) + b\ln^2(\sigma_2/\sigma_1) + c\ln(m_2/m_1)\right]}{1 + \rho_1^{*3.0}\left[d\ln(\sigma_2/\sigma_1)\right]^2} \tag{8}$$

where coefficients a, b, c and d are linear functions of the reduced number density of solvent:

$$\begin{cases} a = -1.676382\rho_1^* + 1.638561 \\ b = -8.516830\rho_1^* + 8.631536 \\ c = -1.320347\rho_1^* + 1.351067 \\ d = -5.062546\rho_1^* + 5.409662 \end{cases} \tag{9}$$

and F_{11} is calculated according to Ruckenstein and Liu [31]:

$$F_{11} = 1 + 0.94605\rho_1^{*1.5} + 1.4022\rho_1^{*3} - 5.6898\rho_1^{*5} + 2.6626\rho_1^{*7} \tag{10}$$

The softness of the repulsive interactions should be now introduced. This may be accomplished by perturbation approaches, which usually combine HS models as an appealing and tractable first approximation, for the major excluded-volume and packing effects, with an effective diameter dependent on temperature and possibly on density, to account for the softness of the repulsive potential. Following Liu *et al.* [23, 32] and the extensive comparison carried out by Silva *et al.* [12], the selected expression is only $T-$ $-$dependent:

$$\sigma_{i,\text{eff}}\left(T_i^*\right) = \sigma_{i,\text{LJ}} \times 2^{\frac{1}{6}}\left[1 + \left(1.3229\,T_i^*\right)^{\frac{1}{2}}\right]^{-\frac{1}{6}}, \qquad i = 1,2,12 \tag{11}$$

Note that i = 1 or 2 for pure solvent and solute, and 12 for the binary system. According to Eq. (5), the calculation of $g(\sigma_{12,\text{eff}})$ needs $\varphi_{1,\text{eff}} = \frac{\pi}{6}\rho_1\sigma_{1,\text{eff}}^3$, and effective diameters

$\sigma_{1,\mathrm{eff}}$ and $\sigma_{2,\mathrm{eff}}$; additionally, F_{12} (Eq. (8)) also needs $\sigma_{1,\mathrm{eff}}$ and $\sigma_{2,\mathrm{eff}}$; on the contrary, Eq. (1) uses $\sigma_{12,\mathrm{eff}}$. The implied reduced temperatures are:

$$T_i^* \equiv k_\mathrm{B} T / \varepsilon_{i,\mathrm{LJ}} \ , \qquad\qquad i = 1,2,12 \tag{12}$$

where the binary LJ diameter and energy are evaluated by the classical Lorentz-Berthelot combining rules given by Eqs. (2) and (13), respectively.

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \sqrt{\left(\varepsilon_{1,\mathrm{LJ}} / k_\mathrm{B}\right) \times \left(\varepsilon_{2,\mathrm{LJ}} / k_\mathrm{B}\right)} \tag{13}$$

The LJ force constants may be taken from Table 7 of Liu *et al.* [32] or, for substances not covered in that essay, calculated by the following corresponding states correlations of Silva *et al.* [22] (critical constants in K and bar):

$$\sigma_\mathrm{LJ}^3 (\text{Å}^3) = 0.17791 + 11.779 \left(\frac{T_\mathrm{c}}{P_\mathrm{c}} \right) - 0.049029 \left(\frac{T_\mathrm{c}}{P_\mathrm{c}} \right)^2 \tag{14}$$

$$\frac{\varepsilon_\mathrm{LJ}}{k_\mathrm{B}} (\mathrm{K}) = 0.774 T_\mathrm{c} \tag{15}$$

Eq. (14) may be adopted successfully for $T_\mathrm{c} / P_\mathrm{c} < 100$. For higher values, one may estimate LJ diameter by a relation provided by principles of corresponding states [13, 33-34], $\sigma_\mathrm{LJ} (\text{Å}) = 0.809 V_\mathrm{c}^{1/3}$, where V_c is critical volume in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$.

Let us now analyse the attractive forces. According to Kushick and Berne [35] and Straub [36], such forces play an important role in the transport process, especially at low temperatures. Several functions have been proposed in literature to take them into account in order to derive models for the LJ fluid (*e.g.* Straub [36], Speedy *et al.* [37]). In this work an exponential factor has been selected to embody such attractive contribution:

$$D_{12,\mathrm{LJ}} = D_{12,\mathrm{E}} \times F_{12} \times \exp\left(-\frac{\alpha_{12}}{T_{12}^*} \right) \tag{16}$$

The desired correlation for the tracer diffusion coefficient of real systems, $D_{12,\mathrm{Real}}$, can be now obtained by writing Eq. (16) explicitly as function of T and ρ_1. After carrying out all previous substitutions the final $D_{12,\mathrm{Real}}$ model arises:

$$D_{12,\mathrm{Real}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{3}{8\rho_1\sigma_{12,\mathrm{eff}}^2}\left(\frac{k_\mathrm{B}T}{2\pi m_{12}}\right)^{1/2}\times\frac{F_{12}}{g\left(\sigma_{12,\mathrm{eff}}\right)}\times\exp\left(-\frac{E_\mathrm{D}}{\Re_\mathrm{g}\,T}\right) \qquad (17)$$

where $\Re_\mathrm{g}=8.31541\times10^7\ \mathrm{erg\cdot mol^{-1}\cdot K^{-1}}$ is the universal gas constant, and $E_\mathrm{D}\equiv\left(\varepsilon_{12,\mathrm{LJ}}/k_\mathrm{B}\right)\alpha_{12}/\Re_\mathrm{g}$ is the unique parameter involved, which only depends on the binary system and can be fitted to experimental data. So, our model may be presented in condensed notation like $D_{12,\mathrm{Real}}=D_{12,\mathrm{Real}}\left(T,\rho_1;E_\mathrm{D}\right)$. For clarity, in Figure 1 the entire calculation procedure is schematically represented.

4.PIII.3. Models Adopted for Comparison

In this paper five tracer diffusivity models were adopted for comparison. They are the hydrodynamic expressions of Wilke-Chang (WC), Lusis-Ratcliff (LR), and Lai-Tan (LT) with zero parameters [3, 13]; the predictive equation of Zhu *et al.* (Zhu) [38]; and the 2−−parameter correlation of Dymond (DHB) [1-2, 39]. In the following, their expressions are summarily presented.

4.PIII.3.1. Wilke-Chang equation [3, 13, 40]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=7.4\times10^{-8}\frac{T\sqrt{\phi_1 M_1}}{\eta_1 V_{\mathrm{bp},2}^{0.6}} \qquad (18)$$

where ϕ_1 is a dimensionless association factor of the solvent, (for CO$_2$, $\phi_1=1$), η_1 is the solvent viscosity (cP); M_1 is solvent molecular weight ($\mathrm{g\cdot mol^{-1}}$); $V_{\mathrm{bp},2}$ is solute molar volume at its normal boiling point ($\mathrm{cm^3\cdot mol^{-1}}$).

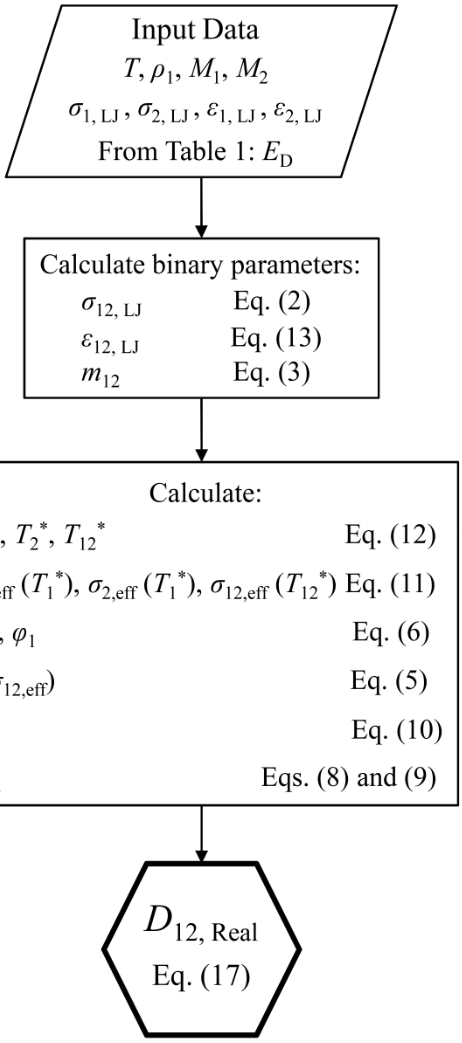

Figure 1. Calculation procedure of new model.

4.PIII.3.2. ***Lusis-Ratcliff equation*** [3, 41]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{8.52\times10^{-8}\,T}{\eta_1\,V_{\mathrm{bp},1}^{1/3}}\left[1.40\left(\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)^{1/3}+\left(\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)\right] \tag{19}$$

4.PIII.3.3. ***Lai-Tan equation*** [42]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=2.50\times10^{-7}\,\frac{T\sqrt{M_1}}{\left(10\times\eta_1\right)^{0.688}V_{\mathrm{c},2}^{\;\;1/3}} \tag{20}$$

4.PIII.3.4. Model of Zhu et al. [38]

$$
\begin{aligned}
D_{12} = {} & \frac{3}{8\sqrt{\pi}}\sqrt{\frac{\sigma_{12,\mathrm{LJ}}^{2}\,\varepsilon_{12,\mathrm{LJ}}}{m_1}}\,\frac{\sqrt{T_{12}^{*}}}{\rho_{12}^{*}}\left(1-\frac{\rho_{12}^{*}}{1.029079\,T_{12}^{*\,0.165377}}\right)\\
& \times\left[1+\rho_{12}^{*\,0.126978}\left(\frac{0.596103\left(\rho_{12}^{*}-1\right)}{0.539292\left(\rho_{12}^{*}-1\right)+T_{12}^{*\left(0.400152-0.41054\rho_{12}^{*}\right)}}+0.68856\right)\right]\\
& \times\exp\left(-\frac{\rho_{12}^{*}}{2\,T_{12}^{*}}\right)
\end{aligned}
\qquad (21)
$$

Here, T_{12}^{*} is calculated as before, but distinct reduced density is introduced, as $\sigma_{12,\mathrm{LJ}}$ is implied instead of $\sigma_{2,\mathrm{LJ}}$:

$$
T_{12}^{*}=\frac{T}{\varepsilon_{12,\mathrm{LJ}}/k_{\mathrm{B}}}\ ,\qquad \rho_{12}^{*}=\rho_1\sigma_{12,\mathrm{LJ}}^{3} \qquad (22)
$$

The combining rules adopted to determine binary parameters are:

$$
\begin{aligned}
& \frac{\varepsilon_{12,\mathrm{LJ}}}{k_{\mathrm{B}}}=\sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}\right)\times\left(\varepsilon_{2,\mathrm{LJ}}/k_{\mathrm{B}}\right)}\\
& \sigma_{12,\mathrm{LJ}}=\left(1-k_{12}^{\mathrm{d}}\right)\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2}\ ,\qquad \text{where } k_{12}^{\mathrm{d}}=0.7926\frac{\sigma_{2,\mathrm{LJ}}-\sigma_{1,\mathrm{LJ}}}{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}
\end{aligned}
\qquad (23)
$$

The LJ parameters for the solvent and solute are estimated by distinct expressions:

$$
\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}\,(\mathrm{K})=\frac{T_{\mathrm{c},1}}{T_{\mathrm{c},1}^{*}}\left[1+0.47527332\,\rho_{\mathrm{r},1}+\left(0.06300484+0.12374707\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \qquad (24)
$$

$$
\sigma_{1,\mathrm{LJ}}(\mathrm{cm})=\left(\frac{\rho_{\mathrm{c},1}^{*}}{\rho_{\mathrm{c},1}}\right)^{1/3}\left[1-0.0368868\rho_{\mathrm{r},1}+\left(0.00006945+0.01089228\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \qquad (25)
$$

$$
\frac{\varepsilon_{2,\mathrm{LJ}}}{k_{\mathrm{B}}}=\frac{T_{\mathrm{c},2}}{1.313}\qquad \text{and}\qquad \sigma_{2,\mathrm{LJ}}=\sqrt[3]{\frac{0.13\,\varepsilon_{2,\mathrm{LJ}}}{P_{\mathrm{c},2}}} \qquad (26)
$$

Such equations are based on the principle of corresponding states, and on the critical point computed by Johnson *et al.* [43] for the LJ fluid ($P_{\mathrm{c}}^{*}=0.13$, $T_{\mathrm{c}}^{*}=1.313$, $\rho_{\mathrm{c}}^{*}=0.31$).

4.PIII.3.5. Dymond Free-Volume expression [1-2, 39]

This model embodies two adjustable parameters: B is a constant characteristic of the solvent-solute pair and V_{D} is a constant related primarily with the solvent.

$$D_{12} = B\sqrt{T}\left(V_1 - V_{\mathrm{D}}\right) \tag{27}$$

4.PIII.4. Model Validation: Database and Data for the Calculations

In this work the largest database of tracer diffusivities published up till now has been compiled with the purpose to validate the new $D_{12,\mathrm{Real}}$ model. It comprehends 314 systems performing 5421 points, covering gas (37 sytems/422 points), liquid (104 systems/675 points) and supercritical (173 systems/4324 points) mixtures. Table 3.1 (Chapter 3) contains the systems studied, number of data points (NDP), number of systems (NS), reduced ranges of temperature, pressure, and solvent density for each system (reduction performed with critical constants), and data sources. As much as possible, all published data were used. However, systems with data available only in graphical form have been rejected. In Table 3.2 (Chapter 3) the name, molecular formula, CAS number, molecular weight, critical constants (T_{c}, P_{c} and V_{c}) and molar volume at normal boiling point (V_{bp}). All data sources are identified.

Some authors do not report the solvent densities of their data. In these cases they have been calculated by the correlations of Pitzer and Schreiber [44] for CO_2, and Hankinson-Brobst-Thomson [13, 45] for other fluids. Concerning the non-reported viscosities, which are necessary for the hydrodynamic equations adopted for comparison in this work, they have been estimated by the correlations of Mehrotra [46] for liquid hydrocarbons, and Altunin and Sakhabetdinov [47] for carbon dioxide. The unknown molar volumes at normal boiling point were estimated by Tyn Calus equation [13, 48]. The unknown critical constants were estimated by Joback [13, 49-50], Somayajulu [51], Klincewicz [13, 52], Ambrose [13, 53-54], Wen-Qiang [55], and Constantinou-Gani [56] methods.

4.PIII.5. Results and Discussion

Table 1 shows the detailed results obtained with our model – equation (17) / / Figure 1 – and the equations adopted for comparison: the hydrodynamic expressions of

Wilke-Chang (WC) [3, 13, 40], Lusis-Ratcliff (LR) [3, 41], and Lai-Tan (LT) [42] with zero parameters; the predictive equation of Zhu *et al.* (Zhu) [38]; and Dymond's correlation (DHB) [1-2, 39] (2 parameters). Global results are compiled in Table 2.

Concerning the calculation procedure, the new model is explicit and straightforward. One only needs the temperature, solvent density and the diffusive energy specific for each binary system, *i.e.* $D_{12,\mathrm{Real}} = D_{12,\mathrm{Real}}(T, \rho_1; E_\mathrm{D})$. In this work one presents NS = 314 values of E_D in Table 1 In terms of future applications, whenever E_D is unknown, it may be firstly optimized using some data points from literature. It is worth noting this optimization is very simple to carry out, since Eq. (17) may be linearized.

From Table 1 it is possible to emphasize its reliability and accuracy, as it provides systematically low average absolute relative deviations (AARDs) for almost all solvent--solute pairs, whether in gas, liquid or supercritical state. For the 314 systems and 5421 points of the collected database, the grand AARD found is only 4.37% (see Table 2), which makes it a very confident 1-parameter correlation. It should be detached the notable performance achieved for systems whose LJ parameters were calculated using critical constants also estimated: *e.g.* systems containing 1,1′-dimethylferrocene, cobalt(III) acetylacetonate, copper(II) trifluoroacetylacetonate, dibenzo-24-crown-8, ferrocene, $\gamma-$linolenic acid ethyl ester, *N*-(4-methoxybenzylidene)-4-*n*-butylaniline, palladium(II) acetylacetonate, squalene, tetrabutyltin, thenoyltrifluoroacetone, triarachidonin, triolein, ubiquinone CoQ10, vitamin K_1, vitamin K_3. In these cases, the unique properties already known were the molecular weight and boiling point. Note that most group contribution methods available to estimate T_c, P_c and V_c do not comprehend metallic atoms like Co, Fe, Pd, Cu, Sn. Hence, the critical constants have been calculated by Klincewicz [13, 52]. Even so, the AARDs found were surprisingly small for these systems: 1.26 to 9.45 %.

In Figure 2 the calculated diffusivities for gas, liquid and supercritical systems are plotted against their experimental values. The three graphics show a good distribution along diagonal which confirms the new model does not exhibit systematic deviations. This fact, in conjunction with the low global AARDs of Table 2, evidences the potential

Table 1. Calculated results.

System			$D_{12,\text{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ ($\text{erg}\cdot\text{mol}^{-1}$)	AARD	$B \times 10^{7}$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^{3}\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD	AARD
Supercritical Systems											
2,3-dimethylbutane	benzene	11	11.6929	1.34	0.9661	70.08	1.56	7.93	75.95	95.80	44.77
2,3-dimethylbutane	naphthalene	9	13.0408	1.40	0.7527	66.74	1.75	2.41	65.82	82.61	60.31
2,3-dimethylbutane	phenanthrene	11	12.3225	1.91	0.5871	54.23	1.53	5.23	61.35	78.84	72.56
2,3-dimethylbutane	toluene	10	11.9749	1.30	0.9458	77.91	1.79	4.82	72.49	90.48	51.73
carbon dioxide	1,1,1,5,5,5-hexafluoroacetylacetone	15	11.6230	4.36	1.1460	11.05	4.36	23.39	18.95	39.26	32.24
carbon dioxide	1,1'-dimethylferrocene	68	10.6896	2.39	1.2835	11.85	3.67	29.12	12.16	31.02	18.70
carbon dioxide	1,2-dichlorobenzene	15	9.0441	1.75	1.5427	16.61	2.07	10.51	6.89	22.17	17.55
carbon dioxide	1,2-diethylbenzene	15	8.4807	1.99	1.3663	15.06	2.61	11.78	6.19	14.43	17.28
carbon dioxide	1,3,5-trimethylbenzene	24	10.0258	4.60	1.2531	11.01	4.29	13.33	7.27	23.55	19.18
carbon dioxide	1,3-divinylbenzene	15	7.7970	1.20	1.5589	18.35	1.39	12.10	3.74	16.70	16.58
carbon dioxide	1,4-diethylbenzene	15	8.4584	2.66	1.3865	15.72	4.06	11.17	5.65	15.36	18.05
carbon dioxide	15-crown-5	29	6.9828	5.84	0.9986	1.19	5.98	21.17	7.85	21.59	15.09
carbon dioxide	1-naphthol	11	5.8650	2.56	2.1460	24.53	0.88	9.22	5.77	9.17	4.60
carbon dioxide	1-phenyldodecane	15	11.1646	2.43	0.9485	17.21	3.14	26.54	6.96	27.70	47.18
carbon dioxide	1-phenylethanol	15	12.1262	1.70	1.3428	14.22	3.15	11.15	10.31	28.54	25.33
carbon dioxide	1-phenylhexane	15	8.6859	2.03	1.2534	16.08	2.71	14.59	7.52	16.20	23.78
carbon dioxide	1-phenyloctane	15	8.0059	2.72	1.1894	16.53	3.65	20.79	8.65	16.88	27.35
carbon dioxide	1-propanol	17	9.3807	4.61	1.3448	-10.04	3.00	8.71	15.43	26.25	4.49
carbon dioxide	2,2,4,4-tetramethyl-3-pentanone	9	-1.2255	2.90	3.0352	29.08	0.76	24.62	27.01	14.50	20.80

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	2,3-dimethylaniline	15	12.2897	2.19	1.2259	13.77	2.38	12.08	16.04	35.59	33.42
carbon dioxide	2,3-dimethylnaphthalene	3	8.0571	1.18	1.5361	21.43	1.08	10.35	3.66	16.99	18.98
carbon dioxide	2,4-dimethyl-3-pentanone	8	12.2269	3.28	1.7583	25.46	2.33	27.67	29.97	47.89	28.35
carbon dioxide	2,4-dimethylphenol	15	12.5119	2.87	1.1649	8.33	3.63	11.95	9.42	27.40	24.55
carbon dioxide	2,6-dimethylaniline	15	12.7114	3.12	1.1330	8.66	3.34	11.78	11.47	30.25	28.06
carbon dioxide	2,6-dimethylnaphthalene	6	8.6630	4.33	1.1736	10.78	4.24	15.38	7.15	17.98	18.68
carbon dioxide	2,7-dimethylnaphthalene	6	7.7956	4.50	1.5069	19.63	4.50	11.91	6.91	13.01	16.04
carbon dioxide	2-bromoanisole	15	11.4509	2.26	1.2561	12.79	3.66	10.23	16.52	35.12	30.69
carbon dioxide	2-butanone	38	6.2891	1.96	2.0672	16.91	2.60	9.83	5.38	7.75	4.85
carbon dioxide	2-ethyltoluene	15	8.4941	3.30	1.4172	14.72	3.76	9.30	8.95	9.76	10.53
carbon dioxide	2-fluoroanisole	15	10.9097	1.71	1.3944	14.19	2.58	9.93	18.48	35.01	26.66
carbon dioxide	2-heptanone	11	0.0071	4.68	3.4792	32.29	1.83	22.02	30.11	17.77	23.07
carbon dioxide	2-methylanisole	15	10.5104	2.18	1.3055	12.12	2.79	9.69	9.67	26.90	22.89
carbon dioxide	2-naphthol	16	4.8419	4.19	1.9948	21.27	1.73	6.52	7.84	7.67	10.71
carbon dioxide	2-nitroanisole	15	11.2230	1.73	1.2984	15.75	2.39	10.88	11.47	31.20	30.58
carbon dioxide	2-nonanone	10	-2.5576	3.86	2.8331	29.00	2.35	25.05	35.76	21.43	25.20
carbon dioxide	2-pentanone	23	6.2588	1.98	1.7185	12.62	2.52	7.78	4.45	12.64	2.27
carbon dioxide	2-phenyl-1-propanol	15	13.1297	1.70	1.2825	15.24	2.64	15.83	9.72	30.05	30.05
carbon dioxide	2-phenylethanol	15	11.8008	1.90	1.3652	15.18	3.03	10.31	12.10	30.39	26.79
carbon dioxide	2-phenylethyl acetate	15	12.3946	2.52	1.1080	13.22	3.06	13.89	8.63	32.02	36.37

Table 1 (*Continued*)

System			$D_{12,\,\mathrm{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	2-propanol	18	7.0638	3.70	1.5735	-1.37	2.21	7.42	9.57	19.89	7.64
carbon dioxide	3-ethyltoluene	15	8.1446	3.59	1.4175	14.91	4.00	9.82	11.68	7.07	9.09
carbon dioxide	3-nitrotoluene	15	9.9120	2.56	1.3849	14.90	3.96	9.58	4.00	17.91	18.41
carbon dioxide	3-pentanone	39	6.1599	1.62	2.0419	19.27	2.03	9.04	9.48	4.37	4.31
carbon dioxide	3-phenyl-1-propanol	15	11.8564	1.85	1.5158	20.64	2.28	9.50	6.21	26.32	27.20
carbon dioxide	3-phenylpropyl acetate	15	12.2121	2.99	1.0565	12.96	3.37	14.86	7.12	31.18	38.05
carbon dioxide	4-ethyltoluene	15	9.0303	2.81	1.4780	17.40	3.07	8.89	7.46	11.41	12.72
carbon dioxide	4-heptanone	9	-3.1193	2.12	3.1752	27.31	0.47	29.62	36.53	25.01	29.68
carbon dioxide	4-methylanisole	15	12.2670	2.06	1.3473	16.11	3.21	12.16	17.52	35.98	31.81
carbon dioxide	5-nonanone	12	-1.7755	4.82	3.0575	32.15	1.10	25.83	34.31	19.33	20.80
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	8.2774	1.74	1.6033	22.88	3.02	13.60	8.45	14.08	19.41
carbon dioxide	6-undecanone	13	-2.1381	4.55	2.8101	31.76	2.53	27.76	38.53	21.79	20.74
carbon dioxide	acetone	178	7.6727	4.34	2.1316	13.74	5.05	11.71	5.64	12.59	10.29
carbon dioxide	acridine	6	10.0396	2.64	1.2634	16.55	2.85	15.47	4.93	20.98	27.22
carbon dioxide	adamantanone	8	-1.7883	2.59	1.4379	-2.78	2.59	29.47	18.17	7.13	14.95
carbon dioxide	a-linolenic acid	56	8.9849	3.53	0.9745	15.74	2.79	26.31	14.24	18.39	32.29
carbon dioxide	allylbenzene	15	9.2397	3.35	1.3060	10.81	3.34	10.60	5.36	17.71	16.32
carbon dioxide	aniline	15	15.1453	3.04	1.1791	8.61	2.46	21.45	33.34	48.89	33.65
carbon dioxide	anisole	15	10.3116	1.99	1.4822	13.90	2.97	7.70	7.33	22.66	16.31
carbon dioxide	anthracene	22	5.3986	2.71	1.6433	22.35	1.75	20.69	10.38	9.98	14.67

Table 1 (*Continued*)

System			$D_{12,\,\mathrm{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	a-pinene	15	7.4629	3.67	1.7055	21.73	3.83	9.38	7.00	12.54	9.28
carbon dioxide	arachidonic acid (AA)	75	7.3558	5.03	0.8591	13.44	2.51	49.72	9.70	25.84	41.11
carbon dioxide	AA ethyl ester	48	6.6406	0.58	1.1233	23.26	1.17	37.41	15.16	19.76	30.43
carbon dioxide	α-tocopherol	82	6.8389	2.86	0.9419	18.16	2.21	64.17	31.55	4.98	27.17
carbon dioxide	β-carotene	90	7.9366	3.75	0.6748	16.79	2.26	144.58	14.88	33.25	66.19
carbon dioxide	behenic acid ethyl ester	17	5.3588	1.21	1.2263	27.32	0.86	65.88	21.34	14.66	31.30
carbon dioxide	benzene	222	5.9164	7.57	1.4921	-1.03	7.59	11.77	9.14	11.09	9.70
carbon dioxide	benzoic acid	29	8.9295	5.81	1.8170	21.69	6.34	8.54	9.27	23.35	14.24
carbon dioxide	benzyl acetate	15	10.4248	2.11	1.3600	16.99	3.02	9.82	7.79	27.69	28.09
carbon dioxide	benzylacetone	15	11.1435	2.67	1.0795	9.68	3.76	12.63	6.19	27.48	30.46
carbon dioxide	biphenyl	24	8.4650	3.58	1.3557	13.85	3.39	15.21	10.13	10.78	10.04
carbon dioxide	b-pinene	15	5.8642	3.51	1.3716	9.22	4.97	10.14	11.72	7.30	5.08
carbon dioxide	bromobenzene	15	10.2376	4.62	1.4373	12.25	4.36	9.08	7.81	21.50	13.52
carbon dioxide	butyric acid ethyl ester	16	7.2422	3.51	2.2177	27.36	1.89	3.91	4.31	11.80	6.58
carbon dioxide	caffeine	21	14.0214	7.74	0.7164	-17.53	4.87	37.00	22.62	47.40	31.48
carbon dioxide	capric acid ethyl ester	16	6.1850	2.82	1.7729	29.09	1.44	10.56	13.46	11.25	16.75
carbon dioxide	caprylic acid ethyl ester	16	6.9489	2.19	1.7619	26.83	1.67	7.39	10.23	12.15	14.33
carbon dioxide	chlorobenzene	15	10.5647	3.84	1.4476	11.52	3.61	8.91	8.22	21.67	12.35
carbon dioxide	chrysene	4	4.0191	1.89	1.8594	27.80	2.61	43.90	16.16	6.63	18.17
carbon dioxide	citral	15	6.6552	2.94	1.3860	16.29	4.31	10.55	8.63	13.20	11.19

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	cobalt(III) acetylacetonate	38	12.8945	1.49	1.0715	17.87	2.13	125.95	11.53	40.06	47.22
carbon dioxide	copper(II) trifluoroacetylacetonate	12	17.1980	4.48	1.2764	22.66	5.04	72.60	37.09	62.37	52.90
carbon dioxide	cycloheptanone	8	8.7825	2.90	1.8569	23.71	1.85	8.58	24.01	39.72	18.83
carbon dioxide	cyclononanone	8	9.0682	3.10	1.7583	25.46	2.33	10.68	17.62	36.52	22.69
carbon dioxide	cyclopentanone	8	11.3711	1.30	1.8382	18.40	1.03	13.18	20.31	33.53	9.61
carbon dioxide	dibenzo-24-crown-8	28	6.9846	1.72	1.0944	24.24	1.93	99.02	12.73	22.77	51.41
carbon dioxide	dibenzyl ether	15	10.8917	2.62	1.0702	14.04	3.22	15.81	5.32	30.14	38.16
carbon dioxide	diethyl ether	15	10.4661	14.48	1.0474	-26.59	4.98	32.29	11.80	22.80	9.09
carbon dioxide	diisopropyl ether	15	8.5982	10.04	1.0782	-16.29	7.87	29.92	7.14	12.53	11.51
carbon dioxide	diolein	9	5.7684	4.81	0.6769	14.02	1.61	77.97	23.69	22.33	48.58
carbon dioxide	D-limonene	15	6.9199	3.29	1.3735	12.04	4.06	10.49	9.32	10.54	7.22
carbon dioxide	docosahexaenoic acid (DHA)	63	8.1947	2.87	0.9162	18.60	1.63	58.53	7.28	30.05	48.35
carbon dioxide	DHA ethyl ester	65	6.4044	1.10	1.0708	22.09	1.45	48.46	16.73	18.88	31.39
carbon dioxide	DHA methyl ester	17	6.0194	0.86	1.2079	25.70	0.92	52.38	16.76	17.74	32.12
carbon dioxide	eicosapentaenoic acid (EPA)	55	7.6249	3.48	0.9184	16.15	1.79	46.01	7.79	27.28	41.67
carbon dioxide	EPA ethyl ester	48	6.5200	0.68	1.1626	24.23	1.06	36.48	14.98	19.58	29.92
carbon dioxide	EPA methyl ester	17	6.6928	1.40	1.2964	27.43	0.49	37.76	17.37	16.49	30.48
carbon dioxide	ethanol	24	8.0520	2.98	1.9621	6.43	3.21	12.41	11.29	19.52	9.68
carbon dioxide	ethyl acetate	15	10.4849	17.12	0.8254	-49.61	6.71	36.32	12.75	24.58	8.21
carbon dioxide	ethyl benzoate	15	7.3630	4.55	1.8993	27.23	2.94	12.20	3.88	22.01	24.86

Table 1 (*Continued*)

System			$D_{12,\,\mathrm{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	ethylbenzene	15	7.1995	1.83	1.8248	18.85	2.28	9.47	7.44	7.97	4.84
carbon dioxide	eugenol	15	12.5981	2.90	1.3885	20.62	3.58	10.54	17.29	39.19	39.69
carbon dioxide	ferrocene	98	5.4911	3.40	1.2424	6.91	6.35	21.24	17.32	33.15	18.19
carbon dioxide	fluorobenzene	15	10.8771	3.61	1.7808	17.76	4.22	10.40	11.04	23.76	10.83
carbon dioxide	γ-linolenic acid	142	7.5649	5.23	0.8364	9.15	2.15	33.37	7.79	26.40	36.36
carbon dioxide	γ-linolenic acid ethyl ester	41	9.9816	6.34	0.8603	6.15	5.10	43.72	6.92	37.84	23.99
carbon dioxide	γ-linolenic acid methyl ester	52	7.4397	6.33	0.8588	7.53	7.58	47.11	13.41	19.17	19.94
carbon dioxide	hexachlorobenzene	14	6.7978	8.55	0.8331	-12.47	4.18	25.04	10.99	20.34	14.18
carbon dioxide	iodobenzene	15	11.9409	3.14	1.2680	11.18	2.72	11.69	12.21	28.89	22.56
carbon dioxide	*i*-propylbenzene	15	7.1693	2.16	1.6274	17.00	2.00	10.94	9.27	7.60	7.33
carbon dioxide	L-carvone	23	8.4989	3.18	1.6268	23.50	2.57	11.23	3.95	21.17	24.19
carbon dioxide	linalool	15	8.0284	3.27	1.3508	14.09	4.02	11.26	7.24	13.86	10.49
carbon dioxide	linoleic acid	71	9.4472	5.66	0.8351	9.74	3.73	30.68	9.63	25.29	38.00
carbon dioxide	linoleic acid methyl ester	21	6.3307	2.23	1.0645	19.77	1.66	56.92	15.74	16.35	37.24
carbon dioxide	L-menthone	23	7.5505	3.56	1.7676	25.22	2.81	11.73	5.18	15.93	19.79
carbon dioxide	methanol	10	8.0885	3.97	2.1980	1.60	2.14	20.87	16.79	23.92	18.17
carbon dioxide	monoolein	11	9.9118	3.58	0.8199	13.88	1.22	24.17	8.71	29.20	43.52
carbon dioxide	myristic acid ethyl ester	16	5.8944	2.42	1.4546	27.11	2.14	24.88	15.97	13.35	23.65
carbon dioxide	myristoleic acid	42	9.3432	5.62	0.8465	4.77	2.66	25.97	5.68	32.51	31.43
carbon dioxide	myristoleic acid methyl ester	79	11.0829	8.88	0.7247	-15.38	10.07	68.29	10.41	29.12	14.33

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*N*-(4-methoxybenzylidene)-4-*n*-butylaniline	5	-0.5082	1.26	2.1419	29.00	0.33	42.04	17.85	1.84	3.72
carbon dioxide	naphthalene	83	7.9398	8.46	1.4146	11.79	8.29	18.59	10.81	14.62	10.14
carbon dioxide	*n*-butylbenzene	15	8.4175	1.94	1.4109	15.95	2.97	11.18	6.29	13.93	16.57
carbon dioxide	*n*-decane	5	-1.9772	4.28	3.8443	36.48	1.47	32.31	38.51	23.56	21.11
carbon dioxide	*n*-dodecane	5	-2.4436	6.38	4.3507	39.93	2.99	37.54	40.87	24.36	19.59
carbon dioxide	*n*-heptane	5	1.0716	3.79	3.9421	35.67	1.00	20.99	28.91	16.05	18.71
carbon dioxide	*n*-hexane	5	2.6677	3.64	3.9838	35.55	2.09	16.06	22.91	10.85	16.44
carbon dioxide	nitrobenzene	15	10.2898	2.18	1.2975	9.79	3.33	9.96	8.79	24.87	19.22
carbon dioxide	*n*-nonane	5	-1.1931	4.42	4.0604	37.02	1.43	29.33	36.45	22.22	21.11
carbon dioxide	*n*-octane	5	-0.1518	4.51	4.1527	37.05	1.66	25.60	33.41	19.86	20.36
carbon dioxide	*n*-pentane	5	4.5108	4.00	4.0586	35.82	1.67	9.12	13.23	2.52	12.10
carbon dioxide	*n*-pentylbenzene	31	8.3397	1.94	1.6168	21.86	3.95	12.96	8.27	13.58	17.27
carbon dioxide	*n*-propylbenzene	34	9.0653	9.49	0.8647	-17.49	5.03	25.18	12.75	20.46	8.67
carbon dioxide	*n*-tetradecane	5	-2.4383	7.65	4.3703	41.99	3.32	43.05	38.78	19.50	12.24
carbon dioxide	*n*-undecane	5	-2.8335	5.24	4.1553	38.28	1.85	35.87	40.94	25.46	21.81
carbon dioxide	oleic acid	19	9.5105	5.85	0.8088	9.94	2.14	37.36	10.03	26.11	40.02
carbon dioxide	oleic acid ethyl ester	5	11.0841	7.85	0.5458	-23.03	0.97	53.72	5.72	38.56	29.14
carbon dioxide	oleic acid methyl ester	19	12.2814	8.17	0.5031	-34.23	1.93	65.15	6.50	42.07	27.79
carbon dioxide	palladium(II) acetylacetonate	125	13.2440	2.36	1.2460	17.11	4.65	91.51	21.93	44.15	38.05
carbon dioxide	palmitic acid ethyl ester	17	6.4017	1.27	1.3142	26.47	0.61	30.82	15.14	16.97	28.90

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*p*-dichlorobenzene	13	9.6489	3.59	1.5067	16.27	3.72	8.76	10.61	27.05	17.02
carbon dioxide	phenanthrene	19	3.9920	6.18	1.3448	12.04	5.03	23.94	13.96	8.79	6.02
carbon dioxide	phenol	109	9.6578	3.01	1.3641	2.62	4.61	8.02	21.47	33.35	10.35
carbon dioxide	phenylacetic acid	16	8.8548	1.90	1.7122	22.71	1.80	6.41	4.25	22.72	15.84
carbon dioxide	phenylacetylene	15	10.4016	1.13	1.6377	17.26	1.58	7.61	7.80	22.91	16.04
carbon dioxide	phenylmethanol	15	10.5980	1.61	1.5257	16.57	2.54	8.05	13.91	30.10	22.63
carbon dioxide	pyrene	18	5.9952	2.50	1.5497	23.47	1.84	26.23	9.18	13.72	20.83
carbon dioxide	squalene	5	7.0990	4.18	1.9069	36.68	1.87	50.04	13.56	20.60	38.21
carbon dioxide	stearic acid ethyl ester	17	6.4240	1.32	1.2474	26.37	1.03	41.53	16.25	17.77	31.65
carbon dioxide	styrene	15	10.6398	4.00	1.6454	18.93	4.39	8.35	5.38	20.35	14.72
carbon dioxide	*tert*-butylbenzene	15	8.2675	3.73	1.8018	23.59	3.62	9.25	7.92	10.83	14.03
carbon dioxide	tetrahydrofuran	15	10.1526	12.53	1.1871	-22.18	4.99	22.16	15.96	27.07	10.90
carbon dioxide	thenoyltrifluoroacetone	15	9.9795	3.61	1.1938	18.09	3.05	13.70	30.20	53.55	47.64
carbon dioxide	toluene	35	7.2441	4.06	1.6490	11.46	4.14	8.44	5.32	11.84	4.46
carbon dioxide	triarachidonin	27	7.7442	8.26	0.4912	6.85	0.82	149.23	17.49	34.89	70.26
carbon dioxide	trierucin	101	9.6030	9.64	0.3731	-2.73	2.95	146.62	13.57	48.33	82.31
carbon dioxide	trifluoroacetylacetone	15	7.9615	1.83	1.7229	19.57	2.18	6.36	3.74	19.21	11.17
carbon dioxide	trinervonin	38	8.6611	8.67	0.3962	2.77	2.86	163.95	16.62	45.38	83.21
carbon dioxide	triolein	10	9.8300	7.64	0.4442	-1.58	1.26	100.27	11.80	44.11	66.59
carbon dioxide	ubiquinone CoQ10	80	8.6671	5.04	0.6220	16.09	4.09	141.53	13.90	37.98	71.55

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ $(\text{erg}\cdot\text{mol}^{-1})$	AARD	$B \times 10^{7}$ $(\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2})$	V_D $(\text{cm}^3\cdot\text{mol}^{-1})$	AARD	AARD	AARD	AARD	AARD
carbon dioxide	vanillin	15	11.0112	1.87	1.5345	21.13	2.03	10.92	12.64	32.26	24.63
carbon dioxide	vitamin K_1	16	3.4907	4.00	0.8940	16.80	2.22	106.89	27.19	9.60	30.62
carbon dioxide	vitamin K_3	20	6.2302	4.51	1.1807	8.84	2.70	24.21	9.77	12.90	11.31
chlorotrifluoromethane	acetone	10	12.4127	6.13	0.9096	19.58	2.56	5.85	23.27	25.58	23.11
chlorotrifluoromethane	*p*-xylene	8	14.5514	11.17	0.4851	-13.32	2.28	38.21	23.77	21.94	31.30
ethane	1-octene	6	6.1933	5.90	1.2050	12.75	1.40	11.82	4.78	54.05	4.19
ethane	1-tetradecene	9	2.8288	2.30	1.5925	38.24	1.61	18.87	17.61	37.37	5.15
sulfur hexafluoride	1,3,5-trimethylbenzene	10	9.0490	9.65	0.5377	18.96	4.59	14.17	33.06	45.23	32.11
sulfur hexafluoride	benzene	9	7.8833	9.07	0.6679	1.44	10.58	7.33	39.39	47.80	40.59
sulfur hexafluoride	benzoic acid	6	11.9344	4.58	0.6061	40.87	2.61	17.30	149.89	81.32	165.45
sulfur hexafluoride	carbon tetrachloride	6	8.8200	2.57	0.6877	35.40	5.18	13.73	37.99	32.10	50.14
sulfur hexafluoride	naphthalene	5	4.2289	6.03	1.1687	67.42	5.52	11.07	77.19	30.05	111.97
sulfur hexafluoride	*p*-xylene	52	6.1192	7.19	0.5781	19.73	12.41	7.75	23.28	40.99	34.37
sulfur hexafluoride	toluene	11	8.7644	10.84	0.5288	-18.56	9.73	7.21	37.76	49.77	35.50
Liquid Systems											
2,2,4-trimethylpentane	1,3,5-trimethylbenzene	4	18.3560	2.74	1.0142	150.50	0.84	36.05	58.70	63.87	176.33
2,2,4-trimethylpentane	benzene	4	14.3556	1.57	1.1336	145.53	1.61	26.78	48.72	57.73	116.69
2,2,4-trimethylpentane	ethylbenzene	4	17.2713	1.55	0.8035	144.09	1.33	35.01	55.63	61.41	157.33
2,2,4-trimethylpentane	*o*-xylene	4	16.4807	2.39	0.9929	147.66	2.24	29.54	51.64	57.35	149.74
2,2,4-trimethylpentane	*p*-xylene	4	13.5319	2.84	0.7954	140.69	1.94	17.09	35.18	40.13	124.47

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
2,2,4-trimethylpentane	toluene	4	14.5635	1.61	1.0099	144.99	1.58	23.72	43.53	50.09	123.97
cyclohexane	1,1'-dimethylferrocene	5	13.0504	6.63	0.5416	98.23	5.36	219.79	28.45	37.44	191.46
cyclohexane	1,3,5-trimethylbenzene	12	4.2229	11.78	1.1194	101.54	2.42	56.15	26.15	24.98	74.04
cyclohexane	argon	6	-0.4301	6.03	2.6698	96.95	2.44	43.30	21.29	4.19	14.01
cyclohexane	benzene	12	3.4685	8.89	1.4520	101.34	3.04	66.34	25.76	25.20	61.82
cyclohexane	carbon tetrachloride	6	5.5469	5.45	1.3613	102.47	1.11	76.72	6.41	4.69	61.75
cyclohexane	ethane	5	0.8264	7.55	2.0214	100.00	2.40	106.17	25.57	17.12	19.02
cyclohexane	ethylene	5	0.8145	9.28	2.1435	99.75	2.30	102.01	25.19	15.54	14.29
cyclohexane	ethylferrocene	6	12.2874	5.98	0.5775	99.11	5.21	191.79	29.02	38.05	193.21
cyclohexane	ferrocene	5	7.4065	6.67	0.5481	97.15	5.52	71.02	35.44	44.73	183.70
cyclohexane	krypton	6	7.7648	6.00	2.1405	98.04	1.26	66.64	8.49	9.36	8.06
cyclohexane	methane	6	4.3374	4.43	2.8585	99.81	0.68	40.39	28.46	16.26	13.59
cyclohexane	naphthalene	12	3.3398	11.63	1.1611	101.24	2.99	40.63	26.63	24.61	69.07
cyclohexane	phenanthrene	8	4.5913	10.49	0.9775	101.00	4.31	6.34	39.49	34.47	47.00
cyclohexane	*p*-xylene	8	3.4651	12.40	1.2210	100.22	3.88	28.73	40.98	36.91	37.42
cyclohexane	tetrabutyltin	7	10.9921	6.98	0.7438	103.12	2.35	13.61	6.48	8.50	145.59
cyclohexane	tetraethyltin	7	6.2492	7.33	1.0441	102.93	2.16	57.13	5.80	6.36	101.58
cyclohexane	tetramethyltin	7	5.3872	8.22	1.2553	102.25	1.25	94.10	4.80	10.31	81.47
cyclohexane	tetrapropyltin	6	7.7236	7.97	0.8573	102.94	2.10	21.82	4.89	7.53	129.86
cyclohexane	toluene	12	2.6425	11.38	1.3305	100.99	2.85	55.83	26.14	24.07	59.85

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
cyclohexane	xenon	6	3.6475	10.18	1.8186	99.39	1.15	85.28	5.62	13.76	25.48
n-decane	12-crown-4	4	14.9215	4.33	0.5689	183.45	2.87	40.09	24.21	24.33	174.46
n-decane	15-crown-5	4	16.2075	7.28	0.4514	182.06	5.22	22.23	28.12	27.29	204.00
n-decane	18-crown-6	4	16.8132	3.78	0.4654	184.73	3.14	4.80	28.17	27.06	224.00
n-decane	argon	3	11.9514	0.79	1.8070	179.89	0.32	47.60	3.65	28.17	15.91
n-decane	carbon tetrachloride	3	12.3033	2.64	0.7923	183.18	0.14	71.32	17.93	22.49	122.24
n-decane	dicyclohexano-18-crown-6	4	18.8529	1.80	0.3810	185.79	1.16	84.24	27.03	27.14	272.75
n-decane	dicyclohexano-24-crown-8	4	18.8549	1.80	0.3344	185.84	1.71	137.91	29.14	30.64	304.55
n-decane	krypton	3	19.0725	0.39	1.3923	180.80	0.78	69.75	16.32	45.82	45.72
n-decane	methane	3	17.5992	0.91	1.8223	181.67	0.03	46.00	12.44	7.71	18.52
n-decane	*s*-trioxane	4	13.2383	2.37	0.8812	182.90	0.42	50.22	25.93	35.61	112.93
n-decane	tetrabutyltin	4	19.3337	6.66	0.4353	185.39	2.16	20.57	23.40	22.46	216.69
n-decane	tetraethyltin	3	13.7937	6.62	0.5949	183.97	1.42	47.46	19.59	19.92	157.62
n-decane	tetramethyltin	4	14.0521	5.56	0.7287	183.47	1.43	71.35	30.51	36.23	131.15
n-decane	tetrapropyltin	4	16.6352	6.66	0.4903	184.67	1.55	24.65	23.25	22.27	190.08
n-decane	xenon	4	13.5149	2.14	1.1823	181.74	0.62	68.96	23.29	46.08	65.08
n-dodecane	1,3,5-trimethylbenzene	4	15.1196	2.09	0.4609	213.97	0.79	119.21	16.71	13.20	206.98
n-dodecane	acetone	5	17.4902	1.19	0.8244	215.52	1.68	102.53	16.62	23.08	133.34
n-dodecane	benzene	4	15.2967	0.79	0.6766	214.82	1.30	122.54	16.31	18.96	156.36
n-dodecane	carbon dioxide	9	17.7949	3.09	1.2167	210.03	2.20	23.83	10.06	18.79	17.40

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
n-dodecane	carbon monoxide	9	18.0846	7.20	1.4392	212.70	5.90	27.26	17.45	16.32	13.29
n-dodecane	hydrogen	9	34.2553	6.57	3.9660	215.14	5.29	47.80	59.75	44.93	59.39
n-dodecane	linoleic acid methyl ester	4	20.7100	0.53	0.2853	217.39	0.92	41.86	13.66	8.50	335.44
n-dodecane	*m*-xylene	4	13.4291	1.43	0.5477	214.25	1.54	108.51	9.33	7.60	173.92
n-dodecane	naphthalene	5	13.7023	2.07	0.5064	214.04	1.41	81.24	12.27	9.28	183.79
n-dodecane	*n*-decane	5	13.1427	6.85	0.5822	219.24	2.98	29.97	21.54	25.19	80.95
n-dodecane	*n*-hexadecane	5	18.3101	6.69	0.4466	221.99	6.69	19.30	14.84	19.00	130.15
n-dodecane	*n*-octane	9	12.9556	4.16	0.6640	218.97	1.48	25.45	21.35	24.34	62.05
n-dodecane	*n*-tetradecane	5	15.1250	8.76	0.4729	221.14	7.84	17.19	18.00	20.79	114.67
n-dodecane	toluene	4	14.0054	1.47	0.6374	214.93	2.01	110.79	9.90	9.70	159.39
n-eicosane	carbon dioxide	5	30.6951	2.07	0.8724	352.03	2.07	21.16	16.80	21.39	28.22
n-eicosane	carbon monoxide	5	32.4152	2.39	1.0324	354.30	2.43	31.74	19.36	15.23	13.28
n-eicosane	hydrogen	5	53.2444	4.04	3.0212	357.65	4.65	36.80	62.00	45.86	54.06
n-eicosane	*n*-dodecane	5	23.6796	4.55	0.3222	361.84	4.28	60.70	14.60	25.27	139.25
n-eicosane	*n*-hexadecane	5	25.7495	5.52	0.2678	362.04	3.44	55.72	13.47	24.58	169.03
n-eicosane	*n*-octane	5	22.6581	4.66	0.4003	359.67	4.78	56.15	16.80	24.94	103.21
n-heptane	*n*-decane	5	10.7932	3.19	0.9631	132.45	1.65	6.81	34.06	28.81	36.75
n-heptane	*n*-dodecane	5	11.1033	3.08	0.8855	132.67	2.18	15.55	30.61	24.63	55.32
n-heptane	*n*-hexadecane	8	14.0921	3.15	0.7499	133.82	3.09	24.56	33.68	26.86	57.37
n-heptane	*n*-octane	4	9.7681	2.45	1.1427	133.32	1.92	5.00	35.23	30.29	31.76

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
n-heptane	*n*-tetradecane	5	11.2144	3.13	0.8028	133.05	2.96	29.65	29.40	22.68	64.30
n-hexadecane	carbon dioxide	10	31.0751	3.56	0.9379	278.97	1.91	34.82	12.21	24.25	24.16
n-hexadecane	carbon monoxide	10	32.9237	3.06	1.0499	280.25	3.08	51.49	13.21	18.74	15.71
n-hexadecane	hydrogen	10	50.3284	13.34	2.1314	268.40	7.32	37.24	55.28	38.35	49.80
n-hexadecane	*n*-decane	5	25.6504	5.73	0.4751	291.18	6.01	62.45	13.07	19.99	116.34
n-hexadecane	*n*-dodecane	5	25.8228	3.05	0.3976	288.61	2.43	55.76	14.96	20.42	127.81
n-hexadecane	*n*-octane	10	25.5133	5.77	0.5159	289.46	3.65	64.04	13.88	19.16	100.91
n-hexadecane	*n*-tetradecane	5	25.2249	3.73	0.3774	290.23	5.42	42.01	13.59	21.15	139.97
n-hexane	1,1'-dimethylferrocene	4	19.6538	5.75	0.1282	-0.01	5.76	57.06	19.62	32.93	109.75
n-hexane	1,3,5-trimethylbenzene	20	12.4970	4.18	0.8743	101.17	14.54	5.88	48.09	46.33	52.86
n-hexane	acetone	5	11.3525	2.74	1.4801	111.01	3.03	7.37	5.42	20.34	47.08
n-hexane	acetonitrile	7	10.1549	5.17	1.1551	102.14	5.93	22.16	115.32	146.30	185.38
n-hexane	benzene	36	9.8172	6.68	1.1371	103.51	14.54	26.17	80.10	88.03	121.67
n-hexane	carbon disulphide	10	6.4817	6.22	1.1409	102.23	4.66	64.04	178.18	224.06	262.41
n-hexane	ethylferrocene	4	19.2030	5.56	0.1264	-0.01	5.70	45.98	21.26	34.76	112.64
n-hexane	ferrocene	4	14.6000	5.37	0.1382	-0.01	5.47	8.76	28.28	43.09	107.67
n-hexane	indole	4	11.7688	4.11	0.4384	84.37	2.83	10.84	10.40	1.82	64.47
n-hexane	*m*-xylene	5	11.5153	2.71	1.3601	115.15	2.00	5.49	6.24	11.14	70.80
n-hexane	naphthalene	20	11.1684	5.43	0.8828	98.35	15.15	10.14	49.57	46.00	49.62
n-hexane	phenanthrene	15	10.8404	5.07	0.6767	81.65	11.81	12.83	63.76	59.51	42.96

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_\text{D} \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^{3}·mol^{-1})	AARD	AARD	AARD	AARD	AARD
n-hexane	*p*-xylene	17	11.2087	5.76	0.9088	93.68	16.35	8.34	56.45	54.22	49.73
n-hexane	toluene	28	9.7194	6.71	1.0354	102.80	16.17	18.14	78.86	85.17	126.71
n-octane	1,3,5-trimethylbenzene	4	13.7859	0.99	0.8117	148.56	0.28	22.30	8.13	13.36	116.12
n-octane	argon	4	10.9264	1.78	1.9181	142.44	2.94	19.90	2.39	32.43	9.41
n-octane	benzene	4	9.6781	2.17	1.0124	144.89	0.22	16.11	0.98	7.81	66.99
n-octane	carbon tetrachloride	4	12.5805	1.54	1.0157	148.85	0.59	34.74	12.51	20.88	89.67
n-octane	ethyl benzene	4	12.7658	2.95	0.7797	145.55	1.55	22.88	6.06	11.77	101.41
n-octane	krypton	4	17.5478	1.56	1.5181	143.52	2.86	37.40	16.13	46.81	28.78
n-octane	methane	4	15.2991	2.11	2.0640	145.64	2.95	18.87	12.50	8.93	12.26
n-octane	*o*-xylene	4	10.9938	0.74	1.0323	149.57	0.87	13.46	1.66	4.90	88.19
n-octane	*p*-xylene	4	8.9739	0.83	1.0964	149.51	0.86	6.18	8.17	3.28	75.33
n-octane	tetrabutyltin	4	19.2556	3.34	0.5544	150.12	1.13	13.75	16.40	19.86	150.45
n-octane	tetraethyltin	5	15.3481	9.45	0.7116	148.73	6.31	17.69	20.42	24.33	121.38
n-octane	tetramethyltin	4	14.3788	4.89	0.8621	147.09	1.35	36.01	19.45	28.37	90.42
n-octane	tetrapropyltin	4	16.9356	3.89	0.6115	149.11	1.10	8.07	16.00	19.02	132.61
n-octane	toluene	4	10.6104	2.56	0.9051	145.10	1.51	15.73	1.81	5.83	78.27
n-octane	xenon	4	13.3659	1.66	1.3238	145.23	1.84	42.84	20.04	44.22	45.81
propane	1-octene	8	8.2883	2.05	1.5602	57.26	1.91	9.91	7.32	26.64	14.87
propane	1-tetradecene	8	5.8133	2.09	1.3094	58.74	1.92	40.78	16.66	19.75	25.65

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
					Gas Systems						
argon	ethane	9	5.3472	1.20	4.7507	7729.39	1.72	12.61	–	–	–
argon	hydrogen	5	-0.2416	5.44	23.0413	3938.78	2.29	72.01	–	–	–
argon	*i*-butane	8	9.0204	4.68	2.6722	5654.17	1.33	71.90	–	–	–
argon	methane	9	3.2619	3.06	7.7281	8889.20	1.49	22.49	–	–	–
argon	*n*-butane	8	8.2614	3.00	2.8191	6520.36	1.24	67.17	–	–	–
argon	neon	25	1.8476	1.71	10.3605	6724.28	5.46	35.22	–	–	–
argon	propane	9	6.5346	0.93	3.6775	7706.29	0.78	38.79	–	–	–
carbon dioxide	ethylene	48	7.7370	7.19	2.9026	-3.87	4.79	9.12	–	–	–
carbon dioxide	hydrogen	7	1.5266	0.34	19.8027	5898.70	0.28	73.95	–	–	–
carbon monoxide	helium	7	-3.2255	0.51	22.1377	5018.43	0.16	69.03	–	–	–
carbon monoxide	hydrogen	7	-0.4555	0.26	22.1377	5018.43	0.16	70.85	–	–	–
deuterium	hydrogen	5	-2.1082	6.76	34.7676	2840.99	1.14	35.80	–	–	–
ethane	nitrogen	14	5.9819	1.46	4.8313	6847.25	0.95	11.79	–	–	–
ethylene	carbon dioxide	49	5.9946	5.65	3.0975	5.29	3.53	9.95	–	–	–
ethylene	nitrogen	7	4.8917	0.69	5.0043	5395.35	0.38	8.64	–	–	–
helium	hydrogen	17	-3.7257	12.78	49.5883	5467.93	5.16	51.24	–	–	–
krypton	argon	6	6.9846	1.07	5.6514	11563.83	2.91	32.57	–	–	–
krypton	helium	6	2.2108	0.93	22.0575	9617.38	2.38	81.76	–	–	–
krypton	neon	17	6.7151	2.44	9.0618	8120.62	2.92	53.32	–	–	–

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This work: Eqs. (8) – (17))		DHB (Eq. (27))			Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Solvent (1)	Solute (2)	NDP	$E_D \times 10^{-9}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD
krypton	xenon	8	10.6048	1.07	3.3325	13066.53	2.29	9.25	–	–	–
methane	carbon dioxide	10	6.9849	1.75	5.9479	6501.16	1.72	19.26	–	–	–
methane	tetrachloroethene	5	11.9925	0.74	2.8076	7640.69	0.11	110.69	–	–	–
neon	deuterium	5	0.4004	3.80	24.0282	3212.22	1.12	46.96	–	–	–
neon	helium	24	-0.9529	5.87	28.0397	2125.92	1.25	57.07	–	–	–
neon	hydrogen	5	-2.0151	6.68	31.7987	2881.11	0.63	61.10	–	–	–
neon	xenon	6	2.6328	0.96	6.4366	4241.29	0.78	61.51	–	–	–
nitrogen	helium	8	-0.8881	3.09	21.4938	6427.19	2.11	66.53	–	–	–
nitrogen	hydrogen	29	-2.0425	1.53	23.3826	4968.86	1.25	72.28	–	–	–
nitrogen	methane	7	3.2152	2.60	7.4175	6561.84	1.81	18.82	–	–	–
nitrogen	*n*-butane	5	10.1662	7.23	2.6491	3362.34	0.96	75.74	–	–	–
nitrogen	propane	6	9.7514	5.81	3.2798	4492.50	0.74	52.52	–	–	–
oxygen	helium	8	-1.1792	1.69	21.0509	4501.28	1.36	66.70	–	–	–
oxygen	hydrogen	13	-3.1834	2.65	26.2335	6132.89	0.50	72.82	–	–	–
sulfur hexafluoride	cyclohexane	5	10.4738	0.21	1.1504	8141.63	0.12	2.50	–	–	–
sulfur hexafluoride	methylcyclohexane	5	12.2512	0.88	1.1703	10547.92	0.32	11.66	–	–	–
tetrafluoromethane	1,1,1-trichloroethane	5	7.6343	0.80	1.4470	7233.94	0.86	37.93	–	–	–
tetrafluoromethane	tetrachloroethene	5	9.6719	2.42	1.0459	3426.96	0.92	51.75	–	–	–

of our model to represent tracer diffusivities of real molecules: AARD (Gas) = 3.78%, AARD (Liquid) = 5.35%, and AARD (SCF) = 4.32%. Hence, one parameter seems sufficient to reach excellent results for a huge number of systems over wide ranges of temperature and density. In order to emphasize the good performance of the new model over the global range of diffusion coefficients, particularly at low temperatures and high densities where D_{12} is small, a comparison between the calculated and the experimental values of all systems studied is shown in Figure 3 in log-log scale. The thin and almost linear distribution along diagonal highlights the accurate model behaviour.

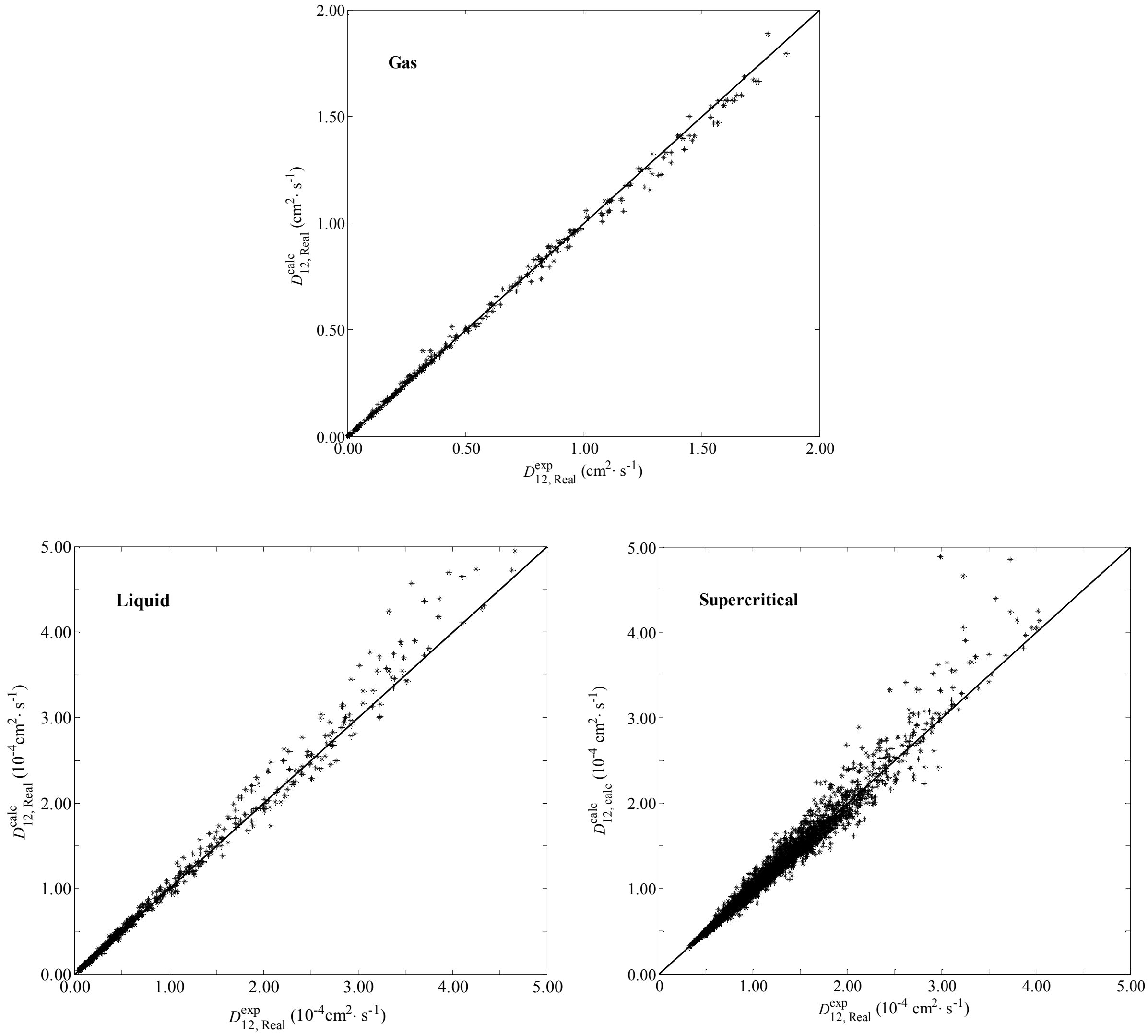

Figure 2. Comparison between calculated and experimental tracer diffusivities for gas, liquid and supercritical systems.

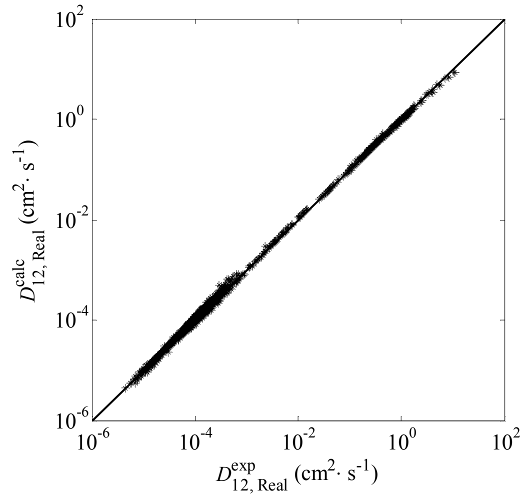

Figure 3. Comparison between calculated and experimental tracer diffusivities for all systems studied in log-log scale.

In Table 2 the global deviations found for the remaining models are listed: $\mathrm{AARD}_{\mathrm{WC}} = 16.47\%$, $\mathrm{AARD}_{\mathrm{LR}} = 26.54\%$, $\mathrm{AARD}_{\mathrm{LT}} = 36.04\%$, $\mathrm{AARD}_{\mathrm{Zhu}} = 37.66\%$, $\mathrm{AARD}_{\mathrm{DHB}} = 3.84\%$. Despite possessing no parameters, the errors offered by the former four equations are not acceptable, particularly those for Lusis-Ratcliff [3, 41], Lai--Tan [42], and Zhu *et al.* [38]. On the other hand, the free volume equation of Dymond [1-2, 39] correlates experimental data very well, which may be attributed in part to the two parameters embodied: B and V_{D} (see Eq. (27)). Nonetheless, its result is comparable to that accomplished by our 1-parameter equation: 3.84 *versus* 4.40%. It is worth to note that the DHB equation presented two physically meaningless results: quite different minimum diffusive free volumes (V_{D}) for the same solvent, which is incorrect, and even negative values (see Table 1). For instance, for CO_2 (solvent) the following V_{D} values have been fitted: -49.61, -34.23,-26.59 $\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}$, etc. Moreover, the DHB equation should be used only for interpolation, which limits its application outside the fitting interval.

Table 2. Relative deviations for the supercritical, liquid and gas systems.

Type of System	NDP	NS	$D_{12,\mathrm{Real}}$ (This work: Eqs. (8) – (17))	DHB (Eq. (27))	Zhu (Eqs. (21) – (26))	WC (Eq. (18))	LR (Eq. (19))	LT (Eq. (20))
Supercritical	4324	173	4.32	3.77	36.98	13.76	24.88	27.28
Liquid	675	104	5.35	5.27	40.53	33.85	37.16	92.15
Gas	422	37	3.78	2.33	39.95	–	–	–
Global	5421	314	4.40	3.84	37.66	16.47	26.54	36.04

The prediction capability of our model has been also tested in this paper and compared with DHB performance according to the following procedure: *i*) 118 systems containing experimental data at distinct temperatures have been chosen in order to fit E_D (new model), and B and V_D (DHB model) to the highest temperature data; *ii*) The parameters so obtained were subsequently used to estimate the tracer diffusivities by the new model and by DHB equation for the remaining lower temperatures. The results evidenced that the DHB prediction capacity is questionable since its AARD for prediction is 15.74%, whereas our new model only rises up to 5.27%. (Remember that the initially calculated deviations for complete correlation were 3.84 and 4.40%, respectively – see Table 2). Table 3 summarises this comparison. Furthermore, the V_D values fitted to all data and to part of them vary too much, as Figure 4 points out. Inclusively, some V_D values jump from positive to negative and vice-versa. In contrast, our E_D values remain approximately the same as Figure 5 illustrates.

Table 3. Average absolute relative deviations calculated for: *i*) correlation of the complete database (the same global values of Table 2); *ii*) estimation of the diffusivities using parameters fitted only to the set of data at highest temperatures. Comparison accomplished for 118 systems/3665 points.

Model	AARD (all data fitted)	AARD (partial fitting)
DHB	3.84	15.74
New Model	4.40	5.27

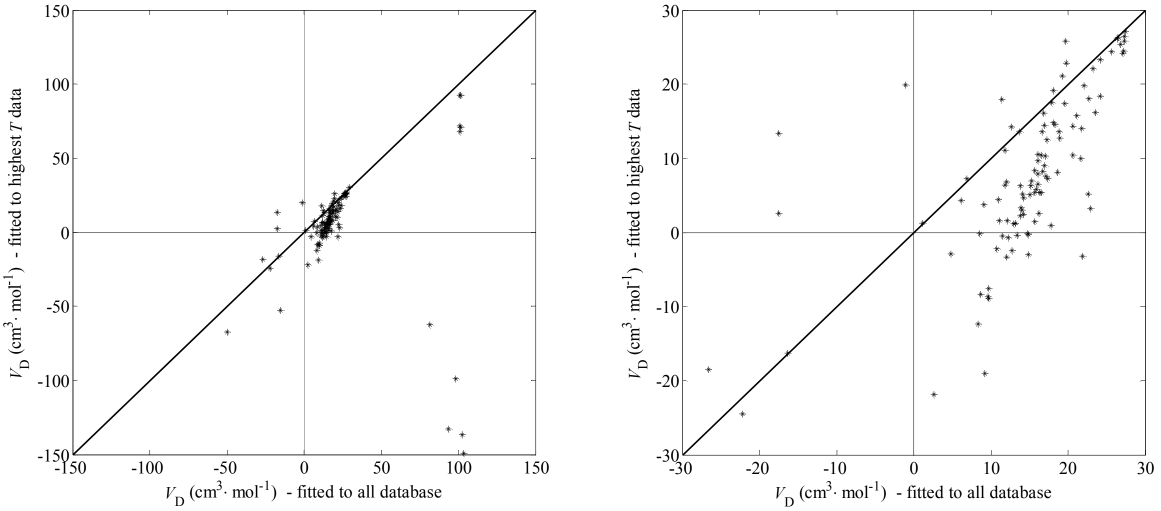

Figure 4. V_D parameter of DHB model (Eq. (27)) regressed using all database *versus* V_D fitted to data at only the highest temperature. Note the different scale of the two graphs (118 systems studied totalizing 3665 experimental points).

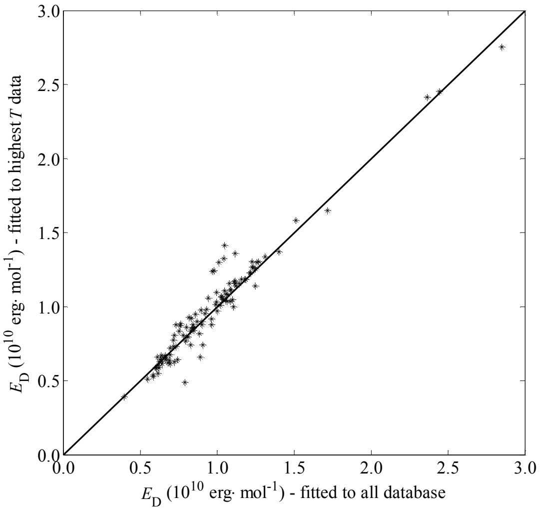

Figure 5. E_{D} parameter of our new model regressed using all database *versus* E_{D} fitted to data at only the highest temperature. (118 systems studied totalizing 3665 experimental points).

4.PIII.6. Conclusions

In this work a new model for tracer diffusion coefficients of real systems is proposed. It was derived on the basis of the HS model fluid, following a systematic derivation whereby the softness of repulsive interactions and the contribution of attractive forces were taken into account by means of the effective hard sphere diameter method and by coupling an Arrhenius exponential term. The model is explicit and straightforward: the diffusion coefficient is computed as function of temperature and density, and calls a diffusive parameter E_{D}, *i.e.* $D_{12,\,\mathrm{Real}} = D_{12,\,\mathrm{Real}}\left(T, \rho_1;\ E_{\mathrm{D}}\right)$. This parameter can be obtained by linear optimization. The validation of the model has been accomplished with the largest data base ever compiled up till now, composed of 314 binary systems and 5421 experimental tracer diffusivities. All properties for the 205 molecules involved were collected and presented here. The new model provides very good results for gas, liquid and supercritical systems over wide ranges of temperature and density, giving rise to a global average absolute relative deviation of only 4.40 %. It also offers excellent representations for systems whose critical constants necessary for the calculation of LJ energy and diameter had to be estimated previously. Finally it must be emphasized its good prediction capability.

Nomenclature

AARD	Average absolute relative deviation, $\mathrm{AARD} = \dfrac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left| \left(D_{12,\mathrm{Real}}^{\mathrm{calc}} - D_{12,\mathrm{Real}}^{\exp} \right) / D_{12,\mathrm{Real}}^{\exp} \right|_i$, %
B	Parameter in Eq. (27)
D	Diffusion coefficient, $\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
F	Correction factor of HS system
$g(\sigma)$	Radial distribution function at contact
HS	Hard sphere fluid
k_B	Boltzmann constant, 1.380658×10^{-16} $\mathrm{erg} \cdot \mathrm{K}^{-1}$
m	Mass of a molecule, g
M	Molecular weight, $\mathrm{g} \cdot \mathrm{mol}^{-1}$
MD	Molecular Dynamics
NDP	Number of data points
NS	Number of systems
N_a	Avogadro constant, 6.0221367×10^{23} mol^{-1}
P	Pressure, bar
$\Re_\mathrm{g}$	Gas constant, $8.31541 \times 10^{7} \mathrm{erg} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$
T	Temperature, K
V	Molar volume, $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
V_D	Parameter in Eq. (27)

Greek letters

η	Viscosity, cP
φ_1	HS packing fraction of solvent
ρ	Number density, N_a/V, cm^{-3}
ε/k_B	Lennard-Jones energy parameter, K
σ	Molecular diameter, cm

Subscripts

bp	Boiling point
c	Critical property
eff	Effective hard sphere diameter (EHSD)

E	Enskog
HS	Hard sphere fluid
LJ	Lennard-Jones fluid
R	Reduced property
Real	Refers to real systems
1, 11	Solvent
2	Solute
12	Binary property

Superscripts

0	Ideal gas
*	Reduced quantity

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Paper IV

Adapted from

Tracer Diffusion Coefficients of Polar Systems

Chemical Engineering Science, **2012**, 73, 151–168.

Abstract

A new model for tracer diffusion coefficients of real polar and non-polar systems is proposed in this work. It is based on the Rice and Gray approach applied to the Stockmayer potential. The new expression embodies three friction coefficients to take into account a repulsive hard sphere core, a soft Lennard-Jones contribution, and a specifically polar interaction term. The model is explicit on temperature and density, and requires only two parameters. The validation was accomplished with the largest database ever compiled – 211 binary systems and 3463 data points – giving rise to an average absolute relative deviation (AARD) of 3.65%. In the particular case of systems with polar solvents – the main objective of this essay – very accurate results were also obtained: AARD = 4.27% for 141 systems and 1994 experimental points. The predictive capability of the new model was also evaluated, exhibiting good and reliable behaviour. A spreadsheet for D_{12} calculation is provided.

4.PIV.1. Introduction

Transport coefficients are key parameters for the design and scale-up of rate controlled separations and multiphase reactors. In the case of binary mixtures, the application of Fick's law is common practice, whereas concentrated multicomponent solutions require more complex approaches as that of Maxwell-Stefan [1-2]. The convective processes also need diffusivity values to estimate the necessary convective mass transfer coefficients via *e.g.* dimensionless correlations for the Sherwood number and *j* factors (*e.g.*, Bird *et al.* [3], Cussler [4]).

Whatever the case, the tracer diffusion coefficients, D_{12}, are particularly important, since mixing rules such as those of Darken [5], Vignes [6], or others reviewed by Pertler *et al.* [7], can be applied to predict the necessary coefficients for the real concentrations in solution. Furthermore, if we use Maxwell-Stefan equations to deal with multicomponent systems, D_{12} values are once more needed to calculate pair diffusivities for the mixture concentrations [1-2]. For these reasons, several equations have been suggested for D_{12} (*e.g.*, Liong *et al.* [8], Millat *et al.* [9], Liu and Ruckenstein [10], Liu *et al.* [11], He *et al.* [12], Reid *et al.* [13], Zhu *et al.* [14], Silva and Liu [15], and Magalhães *et al.* [16-17]) but they are generally applicable over modest ranges of temperature and density, or at least specific for a particular state (gas, liquid or supercritical) [8-9, 13, 15]. Moreover, the majority of the tracer diffusion models found in literature fails to represent polar systems, particularly those with hydrogen-bonding solvents [9, 13, 15]. This fact is a strong limitation for the accurate modelling of an increasing number of systems/units, as for instance those arising under the concept of biorefinery, where green extractions using alcoholic aqueous solutions, supercritical carbon dioxide modified with polar co-solvents, and ionic liquids are mostly adopted [18-20].

Several approaches to describe diffusion coefficients are available in the literature, as, for instance, free volume theory, hydrodynamic theory, kinetic theory, the absolute-rate theory of Eyring, and the Rice and Gray approach, and expressions based on idealized fluids (*e.g.*, Hard Sphere, Square Well, Lennard-Jones, Repulsive Lennard-Jones or Weeks-Chandler-Andersen) [9, 15]. In this work, the Rice and Gray approach was utilized to derive a general model for the binary diffusion coefficients of solutes in gas, liquid, and supercritical systems, involving non-polar and/or polar components. It is based on the Einstein equation which relates diffusivity, D, with friction coefficient, ξ [21-22]:

$$D = k_{\mathrm{B}} T / \xi \tag{1}$$

where k_{B} is Boltzmann constant and T is absolute temperature. In order to ensure its application to any system, the new model includes the contribution of three friction coefficients: one for the repulsive core, another one for soft Lennard-Jones forces, and one for polar interactions. The model was validated with a large database, and the results obtained evidence its reliability and accuracy over wide ranges of temperature and density.

4.PIV.2. Development of the New Model

The knowledge of the intermolecular potential of a fluid makes possible the estimation and calculation of its properties. There are potentials in the literature that describe fluid models with more or less approximation to reality. The potential, U, of more realistic systems may be divided into two terms, one purely repulsive and another containing information about the attractive forces:

$$U = U^{\mathrm{H}} + U^{\mathrm{S}} \tag{2}$$

Here superscript H denotes repulsive part, and S the soft attractive part. For the repulsive component one may choose the potential of hard spheres given by:

$$U^{\mathrm{H}} = \begin{cases} \infty, & r \le \sigma \\ 0, & r > \sigma \end{cases} \tag{3}$$

where r is radial coordinate, and σ is particle diameter. For the attractive part, the Stockmayer [23] potential may be adopted:

$$U^{\mathrm{S}} = \begin{cases} 0, & r \le \sigma \\ 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6} - \nu\,\delta(\sigma/r)^{3}\right], & r > \sigma \end{cases} \tag{4}$$

where

$$\nu = \frac{1}{2}\left[2\cos\theta_{\mathrm{a}}\cos\theta_{\mathrm{b}} - \sin\theta_{\mathrm{a}}\sin\theta_{\mathrm{b}}\cos\psi\right] \tag{5}$$

$$\delta = \frac{1}{2}\frac{\mu}{\varepsilon\sigma^{2}} \tag{6}$$

ε is the attractive well depth, θ_{a} and θ_{b} are the angles of inclination of the dipoles axes to the line joining the centres of the molecules, ψ is the azimuthal angle between them, and μ is the dipole moment.

With the intermolecular potential it is possible to calculate the interaction force by $\boldsymbol{F} = -\nabla U$, which implies the following split if Eq. (2) is taken into account:

$$\boldsymbol{F} = \boldsymbol{F}^{\mathrm{H}} + \boldsymbol{F}^{\mathrm{S}} \tag{7}$$

Kirkwood [24] expressed the friction coefficient implied in Eq. (1) by the integral of the autocorrelation function of forces:

$$\xi = \frac{1}{3}\beta\int_0^\infty \langle \boldsymbol{F}(0)\cdot\boldsymbol{F}(\mathrm{t})\rangle dt \tag{8}$$

where $\beta = 1/k_\mathrm{B}T$, t is time, and the angular brackets $\langle\ \rangle$ represent the average over a canonical ensemble at zero time. This autocorrelation function can be decomposed into three different terms though one of them may be neglected. Since the relaxation induced by the soft forces is rapid in comparison to the average time between hard core collisions, such particular correlation should be small [22, 25]. The following expression arises:

$$\langle \boldsymbol{F}(0)\cdot\boldsymbol{F}(t)\rangle \approx \langle \boldsymbol{F}^\mathrm{H}(0)\cdot\boldsymbol{F}^\mathrm{H}(t)\rangle + \langle [\boldsymbol{F}^\mathrm{S}(0)+\boldsymbol{F}^\mathrm{H}(0)]\cdot\boldsymbol{F}^\mathrm{S}(t)\rangle \tag{9}$$

Accordingly, from Eq. (8) the friction coefficient is calculated by:

$$\xi = \frac{1}{3}\beta\left\{\int_0^\infty \langle \boldsymbol{F}^\mathrm{H}(0)\cdot\boldsymbol{F}^\mathrm{H}(t)\rangle dt + \int_0^\infty \langle [\boldsymbol{F}^\mathrm{S}(0)+\boldsymbol{F}^\mathrm{H}(0)]\cdot\boldsymbol{F}^\mathrm{S}(t)\rangle dt\right\} \tag{10}$$

which, in condensed form, may be written as:

$$\xi = \xi^\mathrm{H} + \xi^\mathrm{S} \tag{11}$$

The hard core contribution, ξ^H, takes into account the repulsive interactions and corresponds to the well-known hard sphere term. It can be calculated by modifying the Enskog [25-26] equation with a correction term F [15]:

$$\xi^\mathrm{H} = \frac{8}{3}\rho\,\sigma^2 g(\sigma)\sqrt{\pi m k_\mathrm{B} T}\Big/F \tag{12}$$

where ρ is the number density, $g(\sigma)$ is the radial distribution function at contact, and m is the mass of the molecule. The attraction term was studied by Helfand [25] under the linear trajectory assumption, being given by:

$$\xi^\mathrm{S} = -\frac{(\pi m\beta)^{1/2}\rho}{3(2\pi)^2}\int_0^\infty k^3 U^\mathrm{S}(k)G(k)dk \tag{13}$$

where $U^{\mathrm{S}}(k)$ and $G(k)$ are the spatial Fourier transforms of $U^{\mathrm{S}}(r)$ and $g(r)$, respectively:

$$\begin{aligned} U^{\mathrm{S}}(k) &= \int U^{\mathrm{S}}(r)\exp(i\mathbf{k}\cdot\mathbf{r})d\mathbf{r} \\ G(k) &= \int [g(r)-1]\exp(-i\mathbf{k}\cdot\mathbf{r})d\mathbf{r} \end{aligned} \tag{14}$$

It is worth noting that the Stockmayer potential (Eq. (4)) decomposes into a Lennard-Jones part and a polar term, hereafter denoted by superscripts S,S and S,P, respectively. Subsequently, ξ^{S} can be split according to:

$$\xi^{\mathrm{S}} = \xi^{\mathrm{S,S}} + \xi^{\mathrm{S,P}} \tag{15}$$

The $\xi^{\mathrm{S,S}}$ contribution has been expressed with good approximation by Ruckenstein and Liu [27] as:

$$\xi^{\mathrm{S,S}} = \frac{8}{3}\rho\sigma^2\sqrt{\pi m k_{\mathrm{B}} T}\,\frac{0.4}{T^{*1.5}} \tag{16}$$

With respect to $\xi^{\mathrm{S,P}}$, we propose in this essay an expression grafted on the equation of Brokaw [28] for polar gases:

$$\xi^{\mathrm{S,P}} = \frac{8}{3}\rho\sigma^2\sqrt{\pi m k_{\mathrm{B}} T}\,\frac{\delta^2}{T^{*1.5}} \tag{17}$$

where $T^* = k_{\mathrm{B}}T/\varepsilon_{\mathrm{LJ}}$ is the reduced temperature, and the Stockmayer parameter δ is given by [13, 28]:

$$\delta = 1.94\times 10^3\,\frac{\mu^2}{V_{\mathrm{bp}}T_{\mathrm{bp}}} \tag{18}$$

T_{bp} and V_{bp} are the normal boiling point and molar volume at normal boiling point, respectively.

Taking into account Eqs. (1), (11), (12), and (15) – (17), the model proposed in this paper to represent the tracer diffusion coefficients of polar and non-polar systems is obtained by substituting σ, m, F, δ, T^* by the corresponding binary quantities σ_{12}, m_{12}, F_{12}, δ_{12}, T^*_{12}, and by introducing one binary parameter (A_{12}) in the polar term, $\xi^{\mathrm{S,P}}$. Hence

$$D_{12,\,\mathrm{Real}} = \frac{k_{\mathrm{B}}T}{\frac{8}{3}\rho_1\sigma^2_{12,\mathrm{eff}}\sqrt{2\pi m_{12}k_{\mathrm{B}}T}\left[\frac{g(\sigma_{12,\mathrm{eff}})}{F_{12}} + \frac{0.4 + A_{12}\,\delta^2_{12}}{T^{*\,1.5}_{12}}\right]} \tag{19}$$

Here subscripts 1, 2, and 12 denote solvent, solute, and binary mixture, respectively.

The Stockmayer binary parameter δ_{12} is calculated in terms of the binary dipole moment, μ_{12}:

$$\delta_{12} = 1.94\times10^3\,\frac{\mu^2_{12}}{V_{\mathrm{bp},1}T_{\mathrm{bp},1}} \tag{20}$$

The combining rule devised in this work for μ_{12} is given by:

$$1+\mu_{12} = \sqrt{(1+\mu_1)\,(1+\mu_2)} \tag{21}$$

where μ_1 and μ_2 are the pure dipole moments. It ensures non-zero values for systems containing at least one non-polar compound, which is very common in practice. For instance, all systems containing polar solutes in supercritical carbon dioxide fall in this case.

The soft nature of repulsions requires the use of an effective diameter. The Ben--Amotz-Herschbach expression has been adopted due to the excellent results accomplished [15, 29]:

$$\sigma_{12,\mathrm{eff}} \equiv \sigma_{12,\mathrm{BAH}} = 1.1532\,\sigma_{12,\mathrm{LJ}}\left[1+\left(1.8975\,T^*_{12}\right)^{1/2}\right]^{-1/6} \tag{22}$$

$$\sigma_{i,\mathrm{eff}} \equiv \sigma_{i,\mathrm{BAH}} = 1.1532\,\sigma_{i,\mathrm{LJ}} \left[1+\left(1.8975\,T_i^*\right)^{1/2}\right]^{-1/6} \tag{23}$$

The implied reduced temperatures are:

$$\begin{aligned} T_i^* &\equiv k_\mathrm{B} T / \varepsilon_{i,\mathrm{LJ}} \\ T_{12}^* &\equiv k_\mathrm{B} T / \varepsilon_{12,\mathrm{LJ}} \end{aligned} \tag{24}$$

and the binary Lennard-Jones (LJ) force constants are evaluated by the classical Lorentz--Berthelot combining rules. If an interaction parameter, k_{12}, is introduced in the diameter combining rule, they express as:

$$\sigma_{12,\mathrm{LJ}} = \left(1-k_{12}\right)\frac{\sigma_{1,\mathrm{LJ}}+\sigma_{2,\mathrm{LJ}}}{2} \quad \text{and} \quad \frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right)\times\left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)} \tag{25}$$

The reduced mass of the system is defined by:

$$m_{12} = \frac{m_1\,m_2}{m_1+m_2} \tag{26}$$

The individual LJ parameters are estimated as functions of the critical temperature and molar volume of each component by Ruckenstein and Liu [27] and Reid *et al.* [13]:

$$\begin{aligned} \frac{\varepsilon_{i,\mathrm{LJ}}}{k_\mathrm{B}}(\mathrm{K}) &= \frac{T_{\mathrm{c},i}}{1.2593} \\ \sigma_{i,\mathrm{LJ}}(\mathrm{cm}) &= 0.7889\times10^{-8}\,V_{\mathrm{c},i}^{1/3} \end{aligned} \tag{27}$$

In this work, the radial distribution function at contact is calculated as proposed by Manssoori *et al.* [30]:

$$g(\sigma_{12}) = \frac{1}{\left(1-\varphi_1\right)^3}\left(1-\varphi_1+\frac{2\varphi_1}{1+\sigma_1/\sigma_2}\right)\left(1-\varphi_1+\frac{\varphi_1}{1+\sigma_1/\sigma_2}\right) \tag{28}$$

where

$$\varphi_1 = \frac{\pi}{6}\rho_1 \sigma_1^3 = \frac{\pi}{6}\rho_1^* \tag{29}$$

and $\rho_1^* \equiv \rho_1 \sigma_1^3$ is the reduced number density of the solvent.

The F_{12} factor of the hard sphere fluid is computed by the correlation of Magalhães *et al.* [16] due to the good results provided:

$$F_{12} = \frac{F_{11} + \rho_1^{*1.7}\left[a\ln(\sigma_2/\sigma_1) + b\ln^2(\sigma_2/\sigma_1) + c\ln(m_2/m_1)\right]}{1 + \rho_1^{*3.0}\left[d\ln(\sigma_2/\sigma_1)\right]^2} \tag{30}$$

The coefficients *a*, *b*, *c* and *d* are linear functions of the reduced number density of solvent:

$$\begin{cases} a = -1.676382\,\rho_1^* + 1.638561 \\ b = -8.516830\,\rho_1^* + 8.631536 \\ c = -1.320347\,\rho_1^* + 1.351067 \\ d = -5.062546\,\rho_1^* + 5.409662 \end{cases} \tag{31}$$

and F_{11} is the correction factor for the self-diffusion coefficient of the solvent, which is calculated by the correlation of Ruckenstein and Liu [27]:

$$F_{11} = 1 + 0.94605\rho_1^{*1.5} + 1.4022\rho_1^{*3} - 5.6898\rho_1^{*5} + 2.6626\rho_1^{*7} \tag{32}$$

Notwithstanding the previous lengthy description of our model, one should refer that it is simple and explicit. For clarity, in Figure 1 the entire calculation procedure is schematically represented. Moreover, in Supplemental Material a spreadsheet for D_{12} calculation is also provided.

4.PIV.3. Models Adopted for Comparison

In this paper four models were adopted for comparison. The predictive model of Zhu *et al.* [14], the hydrodynamic expressions of Wilke-Chang [13, 31-32] and Tyn-Calus [13, 33], and the 2-parameter correlation of Dymond [9, 15, 34].

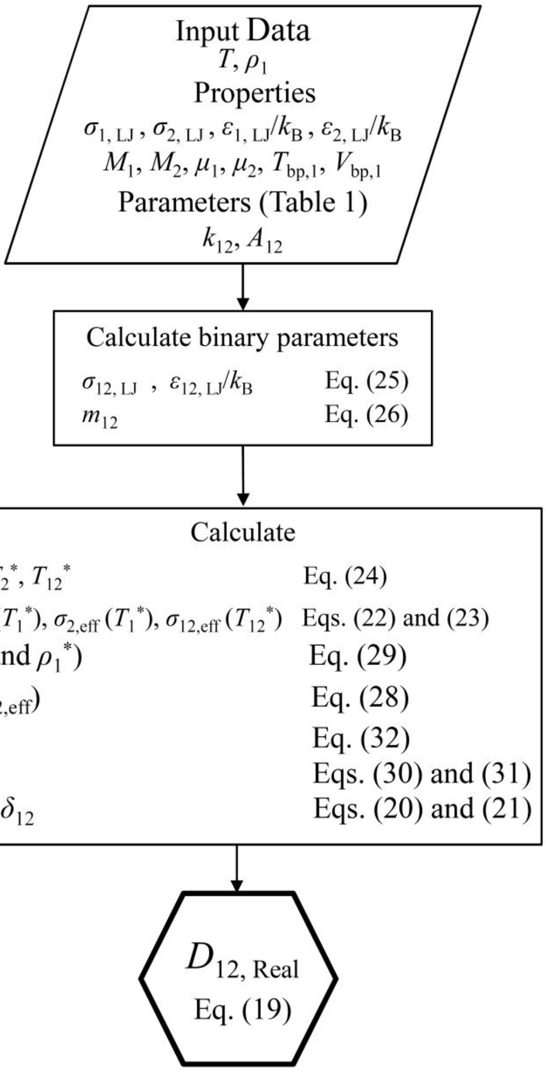

Figure 1. Calculation procedure of the model proposed in this work.

3.PIV.3.1 Model of Zhu et al. [14]

$$
\begin{aligned}
D_{12} = {} & \frac{3}{8\sqrt{\pi}} \sqrt{\frac{\sigma_{12,\mathrm{LJ}}^{2}\,\varepsilon_{12,\mathrm{LJ}}}{m_1}}\,\frac{\sqrt{T_{12}^{*}}}{\rho_{12}^{*}} \left(1 - \frac{\rho_{12}^{*}}{1.029079\,T_{12}^{*\,0.165377}}\right) \\
& \times \left[1 + \rho_{12}^{*\,0.126978} \left(\frac{0.596103\left(\rho_{12}^{*} - 1\right)}{0.539292\left(\rho_{12}^{*} - 1\right) + T_{12}^{*\left(0.400152 - 0.41054\,\rho_{12}^{*}\right)}} + 0.68856 \right)\right] \qquad (33) \\
& \times \exp\left(- \frac{\rho_{12}^{*}}{2\,T_{12}^{*}} \right)
\end{aligned}
$$

Here, T_{12}^{*} is calculated as before (Eq. (24)), but a distinct reduced density is utilized, as $\sigma_{12,\mathrm{LJ}}$ is implied instead of $\sigma_{1,\mathrm{LJ}}$: $\rho_{12}^{*} = \rho_1 \sigma_{12,\mathrm{LJ}}^{3}$. The combining rules used for the binary parameters are the same given by Eqs. (25) and (26), but k_{12}^{d} is:

$$k_{12}^{\mathrm{d}} = 0.7926\,\frac{\sigma_{2,\mathrm{LJ}} - \sigma_{1,\mathrm{LJ}}}{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}} \tag{34}$$

The LJ constants for solvent and solute are estimated by distinct expressions:

$$\varepsilon_{1,\mathrm{LJ}}/k_{\mathrm{B}}(\mathrm{K}) = \frac{T_{\mathrm{c},1}}{T_{\mathrm{c},1}^{*}}\left[1 + 0.47527332\,\rho_{\mathrm{r},1} + \left(0.06300484 + 0.12374707\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{35}$$

$$\sigma_{1,\mathrm{LJ}}(\mathrm{cm}) = \left(\frac{\rho_{\mathrm{c},1}^{*}}{\rho_{\mathrm{c},1}}\right)^{1/3}\left[1 - 0.0368868\,\rho_{\mathrm{r},1} + \left(0.00006945 + 0.01089228\,\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{36}$$

$$\frac{\varepsilon_{2,\mathrm{LJ}}}{k_{\mathrm{B}}} = \frac{T_{\mathrm{c},2}}{1.313} \qquad \text{and} \qquad \sigma_{2,\mathrm{LJ}} = \sqrt[3]{\frac{0.13\,\varepsilon_{2,\mathrm{LJ}}}{P_{\mathrm{c},2}}} \tag{37}$$

Such equations are based on the principle of corresponding states, and on the critical point computed by Johnson *et al.* [35] for the LJ fluid ($P_{\mathrm{c}}^{*} = 0.13$, $T_{\mathrm{c}}^{*} = 1.313$, $\rho_{\mathrm{c}}^{*} = 0.31$).

3.PIV.3.2 Wilke-Chang equation [13, 31-32]

$$D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right) = 7.4\times10^{-8}\,\frac{T\sqrt{\phi_{1}M_{1}}}{\eta_{1}\,V_{\mathrm{bp},2}^{0.6}} \tag{38}$$

ϕ_1 is the dimensionless association factor of the solvent, η_1 is the solvent viscosity (cP), and M_1 is the solvent molecular weight ($\mathrm{g\cdot mol^{-1}}$).

3.PIV.3.3 Tyn-Calus Equation [13, 33]

$$D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right) = 8.93\times10^{-8}\left(\frac{V_{\mathrm{bp},2}}{V_{\mathrm{bp},1}^{2}}\right)^{1/6}\left(\frac{\mathbf{P_1}}{\mathbf{P_2}}\right)^{0.6}\frac{T}{\eta_{1}} \tag{39}$$

P identifies parachors, which are related to the liquid surface tension and may be estimated by additive group contributions. For most organic solvents, an approximation may be used:

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\frac{V_{\mathrm{bp},1}^{0.267}}{V_{\mathrm{bp},2}^{0.433}}\frac{T}{\eta_1} \tag{40}$$

3.PIV.3.4 Dymond Free-Volume expression [9, 15, 34]

This model embodies two adjustable parameter*s*: B is a constant characteristic of the solvent-solute pair, and V_{D} is a constant related primarily with the solvent.

$$D_{12}=B\sqrt{T}\left(V_1-V_{\mathrm{D}}\right) \tag{41}$$

4.PIV.4. Model validation: database and data for the calculations

In this work the largest database of tracer diffusivities of polar and non-polar systems published up till now has been compiled with the purpose to validate the new $D_{12,\ \mathrm{Real}}$ model. It comprehends 211 systems performing 3463 points, from which 141 systems and 1994 points are for polar solvents. Table 3.1 (Chapter 3) contains the systems studied, number of data points (NDP), number of systems (NS), reduced ranges of temperature, pressure, and solvent density for each system (reduction performed with critical constants), and data sources. In Table SD.1 (Supplementary Data) the name, molecular formula, CAS number, molecular weight, critical constants (T_{c}, P_{c} and V_{c}), normal boiling point (T_{bp}), molar volume at normal boiling point (V_{bp}), dipole moment (μ), and LJ force constants are listed for all molecules involved in calculations (157 totally). All data sources are identified.

Some authors do not report the solvent densities of their points, and in these cases they have been calculated by the correlations of Yaws [36], and Cibulka *et al.* [37-39]. Concerning the non-reported viscosities, which are necessary for the hydrodynamic equations of Wilke-Chang and Tyn-Calus, they have been estimated by the correlation of Lucas [40]. In the case of the density and viscosity of water they were estimated by IAPWS [41], and for supercritical carbon dioxide the same properties were estimated by Pitzer and Schreiber [42], and Altunin Sakhabetdinov [43], respectively. The unknown molar volumes at normal boiling point were estimated by Tyn-Calus [13, 44] equation. The unknown critical constants were estimated by Joback [13, 45-46], Klincewicz [13, 47], Ambrose [13, 48-49]), and Wen and Qiang [50] methods. The dipole moments were taken from Reid *et al.* [13] and Yaws [36], and parameters ϕ_1 were taken from [31]. The association factor of water in the original [31] equation is 2.6, but Hayduk and Laudie [51] claimed that 2.26 is better than $\phi_1 = 2.6$.

4.PIV.5. Results and Discussion

Concerning the calculation procedure, the new model is explicit and simple. The required input data are temperature, number density of solvent, normal boiling point of solvent, molar volume at normal boiling point of solvent, and, for both components, the molecular weight, dipole moments, and LJ force constants; the two embodied parameters are k_{12} and A_{12}.The solute and solvent LJ parameters are estimated as a function of T_c and V_c by Eq. (27) (the critical constants can be estimated by appropriate models whenever unknown – see notes on Table 3.2). Therefore, the real diffusivities calculation are accomplished unambiguously according to the dependencies expressed by $D_{12,\mathrm{Real}} = = D_{12,\mathrm{Real}}\left(T, \rho_1; M_1, M_2, T_{\mathrm{bp},1}, V_{\mathrm{bp},1}, \mu_1, \mu_2, \sigma_{\mathrm{LJ},1}, \sigma_{\mathrm{LJ},2}, \varepsilon_{\mathrm{LJ},1}, \varepsilon_{\mathrm{LJ},2}; k_{12}, A_{12}\right)$ – see Figure 1. In Supplemental Material a spreadsheet for D_{12} calculation is provided.

Table 1 shows the detailed results obtained with our model – Eqs. (19) to (32) – and the equations adopted for comparison: model of Zhu *et al.* (Eq. (33)) and the hydrodynamic expressions of Wilke-Chang (Eq. 38) and Tyn-Calus (Eq. (39)) (all with zero parameters), and Dymond correlation (two parameters) (Eq. (41)). The global results are compiled in Table 2.

In the whole, the new model performs accurately, with average absolute relative deviations (AARDs) of only 4.27% for binary systems with polar solvents, and 2.80% for non-polar solvents (see Table 2). The highest deviations found were for 2-propanol/benzene (AARD = 11.57%) and carbon dioxide/ethyl acetate (AARD = = 14.44%) systems (see Table 1), notwithstanding they can be considered small values. These results emphasize that the new model provides very consistent and reliable tracer diffusivities, taking into account the small deviations found for the large database compiled for its validation (211 systems and 3463 data points).

Table 1. Detailed results obtained for the new model and for the equations adopted for comparison.

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ $(\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2})$	V_D $(\text{cm}^3\cdot\text{mol}^{-1})$	AARD	AARD	AARD	AARD
Polar Solvents											
1-propanol	ammonia	31	-3.65824	-153.740	6.09	2.47730	72.620	8.35	-	45.10	14.63
1-propanol	carbon dioxide	27	-0.71744	-4099.800	2.75	3.72410	70.280	3.35	-	51.79	60.25
1-propanol	propane	36	-1.04554	-4416.000	3.27	2.58420	71.340	3.73	-	47.31	50.28
1-propanol	propene	36	-0.94536	-926.540	2.79	2.81220	71.210	3.49	-	50.55	54.27
1-propanol	water	5	-5.90694	-78.944	4.26	1.76510	73.160	2.57	-	155.26	92.89
2-propanol	benzene	10	-0.63235	-2000.100	11.57	2.09850	68.230	10.91	-	10.57	13.02
2-propanol	naphthalene	10	-0.74168	-1700.000	11.25	1.56770	66.860	12.24	-	11.40	15.43
2-propanol	*n*-decane	10	-1.04297	-2132.600	10.29	1.53850	73.370	9.01	-	17.82	13.95
2-propanol	*n*-tetradecane	9	-0.76692	-1709.200	9.25	1.17210	70.600	10.34	-	15.19	17.36
2-propanol	phenanthrene	9	-0.34665	-1041.200	11.20	1.40240	70.770	8.89	-	11.59	18.24
2-propanol	toluene	10	-0.66037	-417.590	11.13	1.90480	68.140	10.62	-	10.78	13.30
2-propanol	water	5	-7.03709	-69.834	1.75	1.70480	74.870	4.96	-	140.59	99.42
acetone	1,2,4-trichlorobenzene	6	0.21125	14.035	0.94	1.68380	63.450	1.26	-	11.48	3.21
acetone	1,3,5-trimethylbenzene	5	0.24201	202.940	0.46	1.77110	63.660	0.40	-	18.98	4.01
acetone	benzene	6	0.25408	354.360	0.35	2.28450	63.640	0.34	-	13.32	6.14
acetone	biphenyl	6	0.18568	149.980	0.41	1.65240	63.910	0.44	-	18.79	1.26
acetone	chlorobenzene	6	0.25829	13.044	0.67	2.00160	63.380	0.88	-	13.58	3.53
acetone	ethylbenzene	6	0.26828	99.133	0.46	1.92950	63.580	0.36	-	19.02	6.48
acetone	naphthalene	5	0.22517	209.020	0.46	1.82060	63.710	0.45	-	18.33	4.04

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
acetone	*n*-propylbenzene	5	0.23700	80.189	0.74	1.80830	63.700	0.72	-	21.10	6.25
acetone	toluene	5	0.27635	108.940	0.40	2.07220	63.500	0.35	-	16.89	6.81
acetone	water	4	0.35109	54.695	0.94	1.88840	58.060	0.87	-	85.11	53.85
acetonitrile	methanol	20	0.95446	4962.700	8.28	2.24880	40.110	4.65	-	17.13	11.78
chlorobenzene	propene	32	0.18741	3361.900	1.23	1.67330	93.740	0.92	-	39.29	33.32
chlorotrifluoromethane	1,3-dibromobenzene	12	0.15507	68.209	5.73	0.41021	-5.894	6.09	-	46.23	27.38
chlorotrifluoromethane	acetone	10	0.40570	49.268	2.41	0.90956	19.580	2.56	-	23.27	29.79
chlorotrifluoromethane	*p*-xylene	8	-0.14963	50.003	8.91	0.48513	-13.320	2.28	-	23.77	22.00
deuterium oxide	oxygen	18	-0.21402	-343.750	4.43	18.09900	17.850	2.28	-	18.03	16.26
ethanol	1,2-butanediol	5	-2.25373	-19.006	1.77	1.84580	55.930	7.82	-	28.71	22.53
ethanol	1,3,5-trimethylbenzene	13	-0.39971	-500.060	6.52	1.93950	49.400	8.04	-	16.75	18.49
ethanol	1,4-butanediol	4	-2.42504	-5.051	1.10	1.62060	55.970	10.88	-	48.41	41.75
ethanol	1-butanol	4	-1.79967	-31.184	1.09	1.85730	55.470	6.05	-	17.42	10.65
ethanol	ammonia	18	-2.19065	-62.308	5.18	3.04440	55.130	4.91	-	41.07	5.92
ethanol	benzene	21	-0.68969	-1153.100	8.73	2.69340	52.540	15.89	-	25.50	22.15
ethanol	benzonitrile	16	-1.15661	-3.628	1.69	2.04180	55.040	1.75	-	25.16	26.84
ethanol	benzyl acetate	15	-0.91862	-16.639	2.95	1.42270	53.740	3.36	-	15.28	13.01
ethanol	carbon dioxide	27	-0.20841	-743.950	4.37	4.40000	52.600	4.80	-	47.62	59.10
ethanol	dibenzyl ether	15	-1.05052	-31.661	3.68	1.44130	54.170	4.00	-	24.76	18.53
ethanol	ethylene glycol	5	-2.33362	-14.952	2.90	1.89450	55.820	7.08	-	59.15	40.71

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
ethanol	glycerol	5	-2.53053	-11.192	1.10	1.74850	56.110	10.35	-	52.51	42.70
ethanol	naphthalene	13	-0.31599	-676.030	6.61	2.00190	48.800	8.18	-	15.36	16.36
ethanol	nitrous oxide	5	-0.30968	-497.950	0.20	4.68930	53.240	0.16	-	44.94	56.73
ethanol	phenanthrene	13	0.46468	2268.400	2.44	1.29560	30.460	4.86	-	10.25	17.44
ethanol	propane	30	-0.80470	-1826.900	2.69	3.50410	54.840	3.92	-	42.67	48.77
ethanol	propene	30	-0.63196	-350.050	3.13	3.78260	54.600	4.22	-	45.33	52.12
ethanol	toluene	14	0.00492	-38.025	6.33	2.19470	46.760	8.99	-	19.00	15.88
ethanol	water	15	-3.85108	-35.140	3.09	3.18560	56.630	8.93	-	143.32	74.14
ethylene glycol	propene	31	0.13158	1179.000	1.53	1.50600	55.160	2.57	-	48.85	50.92
methanol	1,3,5-trimethylbenzene	4	-0.23954	-229.550	2.79	3.62290	37.180	3.45	-	15.85	17.05
methanol	acetonitrile	26	0.62160	26.939	6.24	1.97070	30.410	8.70	-	26.98	38.70
methanol	ammonia	24	-1.07126	-20.870	5.94	4.87170	38.230	5.82	-	112.35	53.10
methanol	benzene	4	-0.17731	-350.160	2.06	4.61480	37.070	3.71	-	9.84	18.77
methanol	carbon dioxide	25	0.09627	-245.000	2.67	9.48670	37.060	3.12	-	30.80	47.80
methanol	carbon monoxide	8	0.51901	5962.400	3.60	5.53790	34.920	3.79	-	15.85	36.13
methanol	naphthalene	4	-0.21985	-335.170	3.01	3.75280	37.120	3.86	-	16.79	18.65
methanol	*p*-chloronitrobenzene	18	-0.33201	-2.946	0.81	3.88600	37.570	0.94	-	22.58	23.72
methanol	phenanthrene	4	-0.24359	-328.330	3.10	3.30240	37.390	2.65	-	19.00	16.64
methanol	toluene	4	-0.15855	-70.610	2.75	4.17170	36.840	4.57	-	14.12	19.89
methanol	water	5	-1.23090	-11.107	1.48	3.89540	37.550	1.72	-	292.96	171.71

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol·cm}^{-1}\text{·s}^{-1}\text{·K}^{-1/2}$)	V_D ($\text{cm}^3\text{·mol}^{-1}$)	AARD	AARD	AARD	AARD
n-butanol	ammonia	64	-3.93570	-278.920	8.40	2.05780	89.730	8.67	-	210.78	157.43
n-butanol	carbon dioxide	66	-0.57025	-4322.600	4.32	2.30330	85.860	4.36	-	21.64	24.82
n-butanol	propane	98	-0.89309	-6499.000	3.10	1.82940	87.620	3.73	-	30.08	29.65
n-butanol	propene	135	-0.86623	-1498.500	3.29	2.11710	87.890	4.52	-	24.82	24.76
water	1,2-butanediol	5	0.27634	-1.470	5.03	20.79200	17.820	11.45	-	2.32	6.92
water	1,3-butanediol	5	0.25840	-1.120	1.07	19.19500	17.790	2.14	-	8.11	0.81
water	1,4-butanediol	5	0.27288	-0.422	4.31	20.81600	17.830	10.60	-	2.41	6.95
water	1-butanol	13	0.24442	-3.473	4.52	22.60500	17.830	9.31	-	3.81	7.93
water	1-pentanol	6	0.24045	-4.394	4.85	24.31700	17.860	12.44	-	6.94	12.84
water	1-propanol	15	0.23117	-3.945	5.78	23.72300	17.820	9.45	-	6.59	7.42
water	2,2-dimethyl-1-propanol	6	0.24439	-4.598	5.15	23.56300	17.860	13.18	-	5.26	11.22
water	2-amino-2-methyl-1-propanol	5	0.29083	-0.587	0.75	17.48200	17.770	1.30	-	6.91	1.39
water	2-methyl-1-butanol	6	0.24630	-3.480	4.28	24.26100	17.870	12.05	-	6.51	12.39
water	2-methyl-2,4-pentanediol	5	0.26789	-0.759	0.61	17.23100	17.810	1.94	-	1.98	1.44
water	2-methyl-2-butanol	6	0.22374	-3.637	4.92	23.44200	17.870	12.76	-	4.13	8.13
water	2-methyl-2-propanol	6	0.20785	-4.195	5.20	20.95000	17.830	9.41	-	7.99	4.13
water	2-pentanol	6	0.26243	-4.171	5.14	23.23900	17.860	13.64	-	5.36	11.30
water	2-propanol	12	0.23212	-4.086	6.62	24.87300	17.830	9.52	-	7.63	7.46
water	3-methyl-1-butanol	6	0.24282	-3.712	4.62	23.41700	17.860	12.61	-	4.72	10.72
water	3-methyl-2-butanol	6	0.24896	-3.548	4.59	24.04900	17.870	12.62	-	5.33	11.28

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
water	3-pentanol	6	0.24986	-4.400	4.56	23.88400	17.870	12.73	-	4.97	10.78
water	acetamide	4	0.11295	-1.395	4.67	50.04600	17.930	8.37	-	7.43	19.39
water	acetone	4	0.40628	0.707	0.93	19.93900	17.680	1.66	-	6.28	15.21
water	ammonia	5	-0.02848	-12.870	2.74	35.21300	17.780	2.43	-	36.59	2.95
water	argon	7	-0.40820	-1249.400	1.67	48.59500	17.900	3.08	-	51.99	10.05
water	benzene	24	0.29281	-157.170	4.62	25.56100	17.820	9.46	-	11.04	19.97
water	benzoic acid	12	0.30948	-8.013	1.11	26.47500	17.860	2.70	-	15.72	20.45
water	biphenyl	7	0.35250	-69.609	1.57	18.84200	17.830	8.56	-	19.93	19.12
water	camphor	8	0.32195	-0.611	1.46	23.85300	17.870	3.84	-	14.43	14.88
water	carbon dioxide	111	0.17358	-454.200	5.17	48.22700	17.840	5.36	-	3.74	25.65
water	cinnamic acid	8	0.29419	-7.651	1.62	34.51900	17.910	3.15	-	27.64	28.41
water	cyclohexane	10	0.24249	-63.301	6.56	25.50000	17.870	10.39	-	7.11	12.94
water	cyclopentane	10	0.21202	-225.740	2.95	26.83400	17.870	7.95	-	4.38	11.66
water	diethylene glycol	5	0.31092	-0.530	0.87	18.90500	17.780	0.80	-	2.86	4.68
water	dimethylethanolamine	5	0.28085	-0.359	1.45	14.66200	17.740	3.18	-	18.36	9.25
water	ethane	16	0.11898	-480.340	6.91	34.77800	17.850	9.04	-	7.15	13.63
water	ethanol	22	0.26134	-3.308	3.44	23.54300	17.750	4.57	-	10.84	7.98
water	ethylbenzene	16	0.31913	-19.161	4.32	19.58200	17.820	10.85	-	9.52	13.20
water	ethylene glycol	9	0.24859	-1.422	1.52	23.02400	17.780	1.81	-	13.69	3.10
water	formamide	4	0.20568	-1.252	5.41	57.66400	17.910	9.03	-	17.86	31.85

Table 1 (*Continued*)

System			$D_{12,\text{ Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
water	galactose	6	0.28446	-0.021	2.48	17.15300	17.850	12.76	-	1.18	0.98
water	glucose	10	0.23409	-0.732	1.67	16.63800	17.840	8.22	-	10.02	7.44
water	glycerol	10	0.25919	-0.976	4.04	21.21500	17.810	7.37	-	6.58	3.80
water	glycine	6	0.26554	-0.033	1.05	24.16500	17.810	2.04	-	2.85	9.10
water	hexafluorobenzene	6	0.30543	-82.741	2.46	18.70700	17.770	4.16	-	4.55	9.85
water	hydrogen sulfide	22	0.31355	-8.739	3.80	28.12200	17.660	5.75	-	8.41	22.44
water	isobutyramide	4	0.12798	-1.387	6.12	43.22300	17.940	10.39	-	10.33	12.94
water	krypton	6	-0.03804	-847.000	1.22	62.56000	17.900	1.90	-	6.33	20.31
water	mannose	6	0.27614	-0.027	2.01	17.28500	17.850	12.23	-	1.81	2.00
water	methane	32	0.01567	-808.650	5.36	39.84900	17.820	5.73	-	7.89	18.76
water	methanol	15	0.20075	-5.635	6.14	33.93600	17.790	6.69	-	6.02	17.61
water	methyl bromide	6	-0.03792	-10.454	1.11	59.83500	17.930	1.90	-	5.26	17.14
water	methyl chloride	6	-0.18564	-11.852	1.15	65.02700	17.940	1.49	-	10.40	12.84
water	methyl fluoride	6	-0.33495	-18.347	3.72	87.36400	17.950	2.14	-	8.93	23.78
water	methylcyclopentane	10	0.23392	-179.270	3.74	23.64600	17.860	10.50	-	4.36	10.77
water	monoethanolamine	5	0.37974	-0.111	2.69	17.90600	17.640	4.50	-	6.69	13.88
water	*N*,*N*-diethylethanolamine	5	0.28714	-0.607	0.41	15.38200	17.780	2.08	-	3.22	1.51
water	naphthalene	7	0.34653	-89.220	2.21	21.35300	17.820	8.56	-	20.50	22.39
water	*n*-butane	16	0.06314	-429.570	7.30	32.40600	17.910	9.89	-	11.19	8.86
water	*n*-butylbenzene	7	0.30747	-26.567	1.82	18.76300	17.840	8.55	-	15.30	14.60

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
water	neon	6	0.00800	-2490.300	1.11	99.39400	17.840	1.81	-	21.76	48.89
water	nitrous oxide	78	0.16596	-193.940	7.55	51.56900	17.860	7.19	-	8.77	24.98
water	*N*-methylpyrrolidone	5	0.32530	-0.257	0.76	19.94700	17.780	2.13	-	4.59	11.13
water	*n*-pentane	8	0.23099	-254.520	7.12	29.66100	17.900	12.01	-	8.36	12.50
water	oxygen	34	0.18456	-487.360	5.63	36.23600	17.750	5.76	-	18.29	14.66
water	pentaerythritol	6	0.28779	-1.000	2.98	16.49800	17.800	10.16	-	2.66	1.28
water	phenol	10	0.46761	4.113	10.65	7.62900	15.810	52.05	-	12.09	4.66
water	piperazine	5	0.30431	-0.320	1.30	14.61600	17.730	3.03	-	13.89	5.73
water	propanamide	4	0.12899	-1.438	6.38	48.15900	17.940	10.44	-	10.72	16.68
water	propane	16	0.11701	-434.350	6.67	34.50000	17.890	9.03	-	7.84	9.73
water	propylene glycol	5	0.27791	-0.466	0.69	22.25900	17.800	0.64	-	9.24	3.10
water	radon	6	-0.03669	-521.430	1.27	52.06100	17.920	1.94	-	14.03	7.89
water	salicylic acid	13	0.35493	-1.038	1.32	27.12300	17.840	3.16	-	24.96	28.35
water	sucrose	10	0.31230	-0.161	1.81	13.10900	17.830	8.82	-	6.14	2.53
water	sulfolane	5	0.35029	-9.251	0.96	19.95000	17.770	2.63	-	7.56	14.68
water	sulfur dioxide	4	0.21889	-8.870	0.32	49.60500	17.860	0.50	-	10.51	29.43
water	tetraethylene glycol	5	0.31313	0.001	0.61	13.56200	17.790	0.64	-	2.31	5.47
water	toluene	15	0.27120	-35.116	5.72	22.17100	17.840	12.32	-	6.36	12.78
water	triethanolamine	5	0.30469	-1.583	0.32	14.62500	17.770	1.51	-	0.52	0.50
water	xenon	6	-0.05513	-659.820	1.31	53.58400	17.910	1.88	-	13.72	10.79

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
water	xylitol	5	0.27396	-1.314	2.36	16.75500	17.820	10.38	-	2.34	2.07
water	xylose	6	0.26993	-0.045	3.13	18.41700	17.850	12.82	-	2.86	0.91
Non-polar solvents											
carbon dioxide	1,2-dichlorobenzene	15	0.29190	23.017	0.81	1.54270	16.610	2.07	10.51	6.89	11.69
carbon dioxide	1,2-diethylbenzene	15	0.22735	1630.300	1.69	1.36630	15.060	2.61	11.78	6.19	6.01
carbon dioxide	1-phenylethanol	15	0.15686	50.219	1.32	1.34280	14.220	3.15	11.15	10.32	17.97
carbon dioxide	1-propanol	17	0.67036	858.690	2.87	1.34480	-10.040	3.00	8.71	15.43	11.60
carbon dioxide	2,4-dimethyl-3-pentanone	8	-0.15013	-6.427	2.21	1.75830	25.460	2.33	24.76	11.25	20.20
carbon dioxide	2,4-dimethylphenol	15	0.30465	188.490	1.95	1.16490	8.328	3.63	11.95	9.42	16.90
carbon dioxide	2-butanone	38	0.10699	1.011	1.57	2.06720	16.910	2.60	9.83	5.38	5.39
carbon dioxide	2-heptanone	11	-0.17692	-15.234	1.69	3.47930	32.290	1.83	22.02	30.11	24.33
carbon dioxide	2-nitroanisole	15	0.19354	1.857	1.43	1.29840	15.750	2.39	10.88	11.47	20.75
carbon dioxide	2-nonanone	10	0.04378	-8.400	2.29	2.83310	29.000	2.35	25.05	35.76	27.22
carbon dioxide	2-pentanone	23	0.13964	5.120	1.83	1.71850	12.620	2.52	7.78	4.45	4.27
carbon dioxide	2-phenyl-1-propanol	15	0.20647	108.720	1.51	1.28260	15.240	2.64	15.83	9.72	19.88
carbon dioxide	2-phenylethanol	15	0.18556	50.958	1.42	1.36520	15.180	3.03	10.31	12.10	19.59
carbon dioxide	2-phenylethyl acetate	15	0.27775	63.562	1.38	1.10800	13.220	3.06	13.89	8.63	22.22
carbon dioxide	2-propanol	18	0.63797	689.430	2.26	1.57350	-1.365	2.21	7.42	9.57	6.96
carbon dioxide	3-nitrotoluene	15	0.13683	0.937	2.18	1.38490	14.900	3.96	9.58	4.00	8.67
carbon dioxide	3-pentanone	39	0.14944	3.305	1.38	2.04190	19.270	2.03	9.03	9.48	6.20

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
carbon dioxide	3-phenyl-1-propanol	15	-0.01116	-12.915	1.60	1.51580	20.640	2.28	9.50	6.21	16.54
carbon dioxide	4-heptanone	9	0.05017	-11.914	0.46	3.17520	27.310	0.47	29.62	36.53	30.93
carbon dioxide	5-nonanone	12	-0.09396	-11.514	1.02	3.05750	32.150	1.10	25.83	34.31	25.24
carbon dioxide	acetone	178	0.05426	-0.398	3.76	2.13160	13.740	5.05	11.71	5.64	5.48
carbon dioxide	acridine	6	0.45449	75.464	1.26	1.26340	16.550	2.85	15.47	4.93	12.06
carbon dioxide	α-linolenic acid	56	0.39740	148.150	2.07	0.97452	15.740	2.79	26.31	14.25	9.32
carbon dioxide	aniline	15	0.23124	116.070	2.56	1.17910	8.609	2.46	21.45	33.34	33.91
carbon dioxide	anisole	15	0.12107	45.069	1.93	1.48220	13.900	2.97	7.70	7.33	11.77
carbon dioxide	α-tocopherol	82	0.39722	24.017	0.89	0.94194	18.160	2.21	64.17	31.55	5.63
carbon dioxide	benzoic acid	29	0.09745	31.650	5.52	1.81700	21.690	6.34	8.54	9.27	13.02
carbon dioxide	benzyl acetate	15	0.13809	20.468	1.91	1.36000	16.990	3.02	9.82	7.79	17.75
carbon dioxide	bromobenzene	15	0.47733	249.930	3.98	1.43740	12.250	4.36	9.08	7.81	10.55
carbon dioxide	butyric acid ethyl ester	16	-0.12509	-29.145	1.89	2.21770	27.360	1.89	3.91	4.31	2.96
carbon dioxide	caffeine	21	0.76727	121.730	3.87	0.71642	-17.530	4.87	37.00	22.62	36.24
carbon dioxide	capric acid ethyl ester	16	-0.02952	-22.901	1.26	1.77290	29.090	1.44	10.56	13.46	3.77
carbon dioxide	caprylic acid ethyl ester	16	-0.04568	-23.606	1.50	1.76190	26.830	1.67	7.39	10.23	4.14
carbon dioxide	chlorobenzene	15	0.40768	227.910	3.02	1.44770	11.520	3.61	8.91	8.22	10.29
carbon dioxide	chrysene	4	0.18503	100.010	0.94	1.85940	27.800	2.61	43.90	16.16	2.80
carbon dioxide	dibenzyl ether	15	0.29629	157.410	1.63	1.07020	14.040	3.22	15.81	5.32	20.72
carbon dioxide	diethyl ether	15	0.75506	4468.200	10.51	1.04740	-26.590	4.98	32.29	11.80	12.38

Table 1 (*Continued*)

System			$D_{12,\,\mathrm{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD
carbon dioxide	diisopropyl ether	15	0.73217	5085.900	7.38	1.07820	-16.290	7.87	29.92	7.14	6.46
carbon dioxide	diolein	9	0.40601	4.566	1.46	0.67686	14.020	1.61	77.97	23.69	9.91
carbon dioxide	D-limonene	15	0.56441	422.740	1.96	1.37350	12.040	4.06	10.49	9.32	4.27
carbon dioxide	ethanol	24	0.24065	69.689	2.71	1.96210	6.431	3.21	12.41	11.29	5.39
carbon dioxide	ethyl acetate	15	0.77334	1440.700	14.14	0.82543	-49.610	6.71	36.32	12.75	13.77
carbon dioxide	ethyl benzoate	15	-0.27764	-29.031	2.47	1.89930	27.230	2.94	12.20	3.88	12.77
carbon dioxide	fluorobenzene	15	0.10752	33.527	3.43	1.78080	17.760	4.22	10.40	11.04	11.16
carbon dioxide	γ-linolenic acid ethyl ester	41	0.80706	1010.000	4.59	0.86030	6.149	5.10	43.72	6.92	27.87
carbon dioxide	iodobenzene	15	0.25991	72.681	2.75	1.26800	11.180	2.72	11.69	12.21	17.69
carbon dioxide	linoleic acid	71	0.45780	523.980	2.91	0.83515	9.744	3.73	30.68	9.63	15.88
carbon dioxide	linoleic acid methyl ester	21	0.33801	57.522	1.45	1.06450	19.770	1.66	56.92	15.74	7.44
carbon dioxide	methanol	10	0.61370	648.410	2.02	2.19800	1.601	2.14	20.87	16.79	7.10
carbon dioxide	monoolein	11	0.36267	190.540	1.07	0.81990	13.880	1.22	24.17	8.71	18.90
carbon dioxide	myristic acid ethyl ester	16	0.02362	-16.895	1.98	1.45460	27.110	2.14	24.88	15.97	4.92
carbon dioxide	oleic acid	19	0.45894	302.320	1.75	0.80876	9.939	2.14	37.36	10.03	16.61
carbon dioxide	oleic acid ethyl ester	5	0.74590	757.860	3.01	0.54585	-23.030	0.97	53.72	5.72	27.68
carbon dioxide	palmitic acid ethyl ester	17	0.03578	-11.887	0.62	1.31420	26.470	0.61	30.82	15.14	8.02
carbon dioxide	phenol	109	0.18750	50.498	2.51	1.35390	2.217	4.66	7.83	21.28	18.04
carbon dioxide	phenylacetylene	15	0.12139	500.000	1.28	1.63770	17.260	1.58	7.61	7.80	12.00
carbon dioxide	phenylmethanol	15	0.07781	10.709	1.55	1.52570	16.570	2.54	8.05	13.91	18.50

Table 1 (*Continued*)

System			$D_{12,\text{Real}}$ (This Work: Eqs. (19) – (32))			DHB (Eq. (41))			Zhu (Eqs. (33) – (37))	WC (Eq. (38))	TC (Eq. (39))
Solvent (1)	Solute (2)	NDP	k_{12}	A_{12}	AARD	$B \times 10^7$ ($\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1/2}$)	V_D ($\text{cm}^3\cdot\text{mol}^{-1}$)	AARD	AARD	AARD	AARD
carbon dioxide	stearic acid ethyl ester	17	0.04484	-17.143	0.67	1.24740	26.370	1.03	41.53	16.25	8.48
carbon dioxide	*tert*-butylbenzene	15	0.09436	10.000	3.10	1.80180	23.590	3.62	9.25	7.92	3.35
carbon dioxide	tetrahydrofuran	15	0.77185	1946.690	8.87	1.18720	-22.180	4.99	22.16	15.96	12.43
carbon dioxide	triolein	10	0.77611	95.281	1.44	0.44421	-1.581	1.26	139.27	26.03	13.52
carbon dioxide	vanillin	15	0.05822	0.468	1.70	1.53450	21.130	2.03	10.92	12.64	21.65
carbon dioxide	water	24	-1.32103	-84.077	9.97	8.32390	36.480	4.18	25.10	56.20	19.65
n-decane	*s*-trioxane	4	-0.13721	10.014	1.99	0.88117	182.900	0.42	50.22	25.93	12.59
n-dodecane	acetone	5	-0.16916	9.998	1.39	0.82437	215.500	1.68	102.53	16.62	3.20
n-hexane	acetone	5	-0.02172	9.991	2.62	1.48010	111.000	3.03	7.37	5.42	5.91
n-hexane	acetonitrile	7	0.27017	1010.000	6.76	1.15520	102.100	5.93	22.16	115.32	110.08
n-hexane	indole	4	0.03093	500.000	4.04	0.43840	84.370	2.83	10.84	10.40	2.18
sulfur hexafluoride	benzoic acid	6	-0.12355	9.979	1.87	0.60607	40.870	2.61	17.30	149.89	76.57
tetrafluoromethane	1,1,1-trichloroethane	5	-0.09665	-13.556	0.78	1.44700	7234.000	0.86	37.93	-	-

In Figure 2 the calculated diffusivities by the new model are plotted against the experimental values. Such plot reinforces the good representation accomplished, as they are essentially located along the diagonal (all points are plotted in the diagram). Moreover, the corresponding relative deviations shown in Figure 3 point out that the new model exhibits an unbiased behaviour, since they are very consistently scattered around zero.

As has been mentioned above, the new model (Eq. (19)) comprehends three contributions: repulsive core $\left(\xi^{\mathrm{H}}\right)$, soft LJ $\left(\xi^{\mathrm{S,S}}\right)$, and polar $\left(\xi^{\mathrm{S,P}}\right)$. Its novelty lies on the embodied $\xi^{\mathrm{S,P}}$ term, which extends the performance of the new model to polar gas, liquid and supercritical systems. It is worth noting that almost all equations in the literature fail to represent polar mixtures, since the intrinsic dipole moments of the molecules are not taken into account, at least properly [9, 15]. The relative importance of each contribution was evaluated by:

$$\frac{100\times\xi^{\mathrm{H}}}{\xi^{\mathrm{H}}+\xi^{\mathrm{S,S}}+\xi^{\mathrm{S,P}}},\ \frac{100\times\xi^{\mathrm{S,S}}}{\xi^{\mathrm{H}}+\xi^{\mathrm{S,S}}+\xi^{\mathrm{S,P}}},\ \frac{100\times\xi^{\mathrm{S,P}}}{\xi^{\mathrm{H}}+\xi^{\mathrm{S,S}}+\xi^{\mathrm{S,P}}}$$

for all data points, giving rise to, respectively: 58.2%, 9.3% and 32.5%. The average results obtained emphasize once more the role played by the hard sphere term (58.2%), and state that the polarity effects cannot be neglected (32.5%).

In Figure 4, the calculated F_{12} corrective factors (Eqs. (30) – (32)) are grouped per type of solvent for all binary systems of the database. Taking into account that F_{12} corrects the Enskog diffusivity to get the corresponding hard sphere value, it is interesting to interpret some of the ranges found in Figure 4. For instance, $F_{12} > 1.1$ in the case of supercritical CO_2, since for intermediate densities computer simulations show that hard sphere diffusivities exceed Enskog predictions [9, 15, 52-53].

On the other hand, in the case of liquid water $F_{12} < 1.0$, since at high densities a backscattering phenomenon appears, whereby particles closely surrounded by a shell of neighbour spheres becomes increasingly locked in and reverses its velocity on collision, which decreases diffusion [15, 52-53].

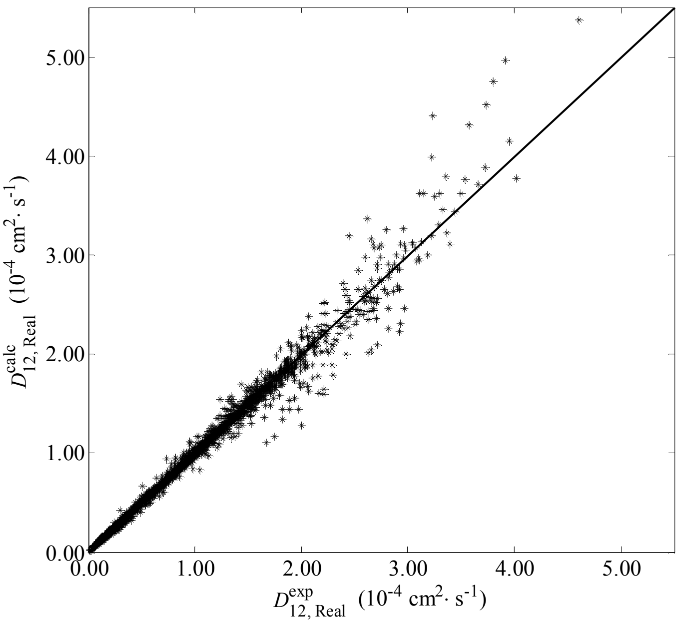

Figure 2. Comparison between calculated and experimental tracer diffusion calculated by the new model.

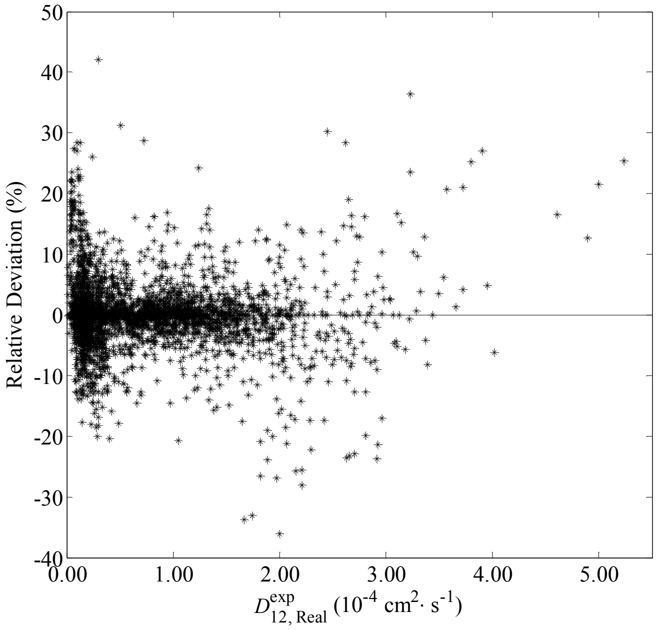

Figure 3. Relative deviations accomplished by the new model as function of experimental diffusivities.

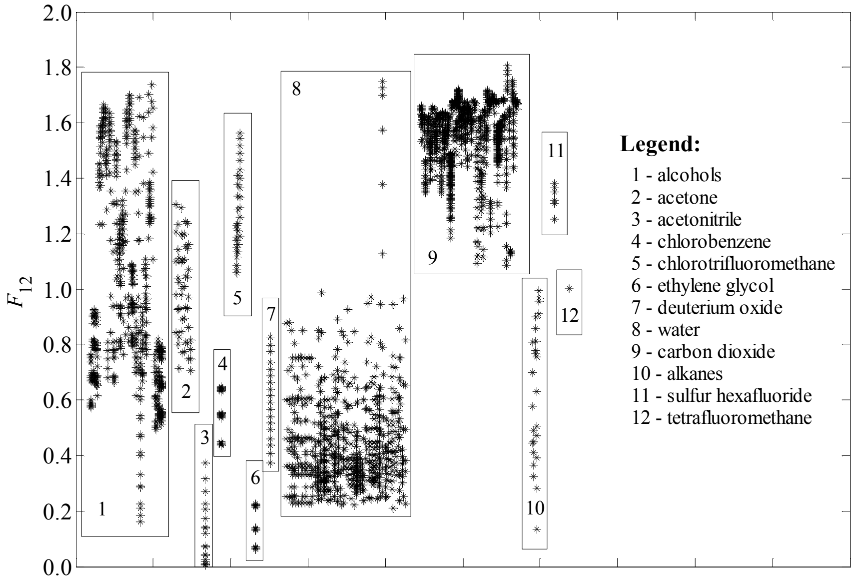

Figure 4. Corrective factors calculated in the new model, grouped per type of solvent for all binary systems of the database.

The new model employs effective hard sphere diameters (σ_{eff}), calculate by the Ben-Amotz and Herschbach expression (Eqs. (22) or (23)), in order to smooth the repulsions of molecules in a real fluid, because they are not rigid impenetrable spheres.

In Figure 5 the reduced effective diameter $\left(\sigma_{\mathrm{eff}}^{*}=\sigma_{\mathrm{eff}}/\sigma_{\mathrm{LJ}}\right)$ dependence upon reduced temperature is shown, being possible to observe its significance. Taking into account how large the effect of a small change in an assigned diameter can be on calculated transport coefficients [15, 53], this figure justifies the improvement attained with effective diameters. In fact, when the tracer diffusivities calculated with $\sigma_{\mathrm{eff}}^{*}$ are graphed against tracer diffusivities obtained without $\sigma_{\mathrm{eff}}^{*}$ (*i.e.*, the diameter is the constant LJ value), huge deviations are found. This is clearly shown in Figure 6.a, where a large number of points lay far from the diagonal. In Figure 6.b it is shown an enlargement of the region near the vertex of Figure 6.a, where the most significant variations were registered. These points are essentially for liquid systems (region of small diffusivities), since in this region the free volume is small and so the impact of diameter becomes bigger.

With respect to the models adopted for comparison, Table 2 points out that the predictive hydrodynamic equations of Wilke-Chang and Tyn-Calus perform poorly with AARD = 23.53% and 22.29%, respectively. In the particular case of polar systems, the deviations get even worst (30.05% and 28.96%). In Figure 7, the deviations attained by the Wilke-Chang equation are shown as function of the experimental diffusivities, in order to detach its weakness for the liquid polar systems under study (please check the large errors in the region of small D_{12}).

On the other hand, the free volume equation of Dymond, with two parameters, correlates experimental data very well (grand AARD = 4.90%). However, as it will be demonstrated next, the Dymond equation should be used only for interpolation, which limits its application outside the fitting interval.

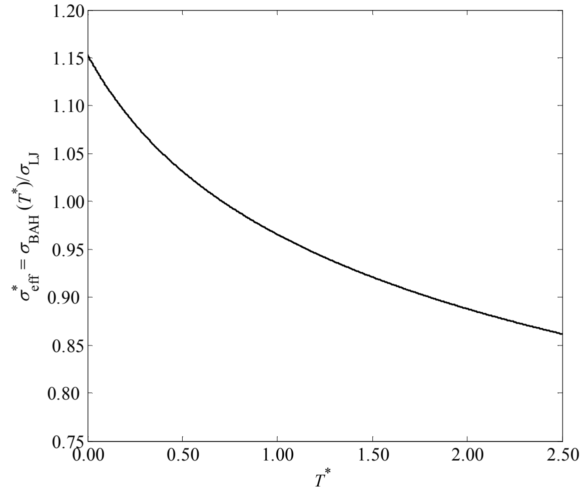

Figure 5. Reduced effective hard sphere diameters *versus* reduced temperature.

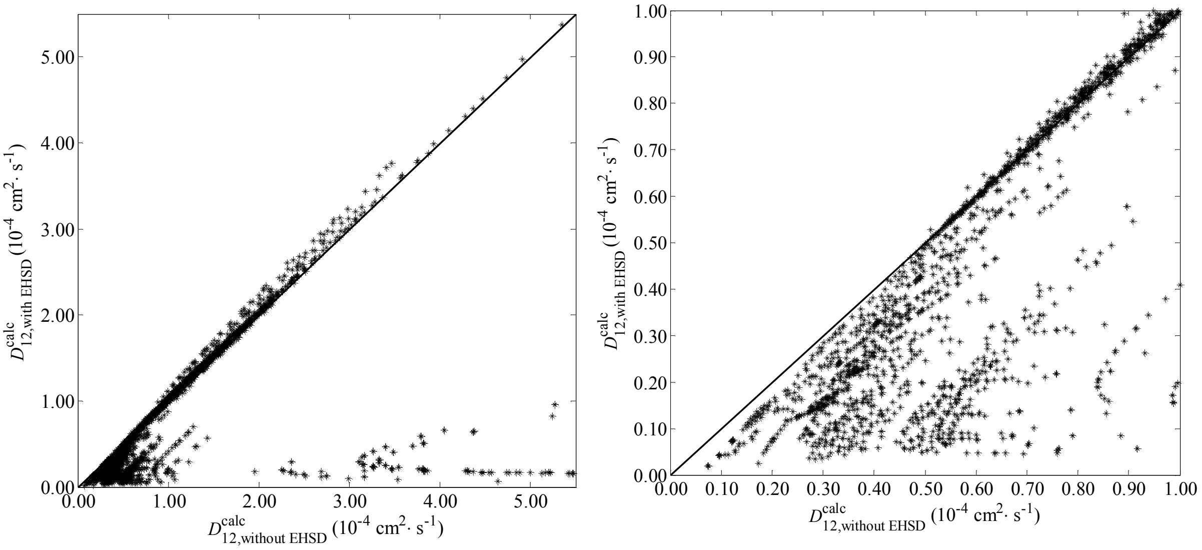

Figure 6. Influence of the effective hard sphere diameter on the calculated tracer diffusivities.

Table 2. Global average absolute relative deviations (AARDs).

Nature of Solvent	NS	NDP	This work	Dymond	Zhu	WC	TC
Polar	141	1994	4.27	6.02	–	30.05	28.96
Non-polar	70	1469	2.80	3.37	21.85	14.66	13.20
Total	211	3463	3.65	4.90	22.85	23.53	22.29

NS = number of systems; NDP = number of data points.

The prediction capability of our model has been also tested and compared with Dymond performance according to the following procedure: *i*) 90 systems containing experimental data (2042 points) at distinct temperatures have been chosen in order to fit k_{12} and A_{12} of new model, and B and V_{D} of Dymond equation to the highest temperatures data; *ii*) the parameters thus obtained were subsequently used to calculate the tracer diffusivities by both expressions at all temperatures. The results shown in Table 3 evidence that the prediction capability of Dymond is questionable, since its grand AARD almost doubles, increasing from 4.90% to 9.20%, whereas our model only increases from 3.65% to 4.66%.

To illustrate the behaviour of our model, several tracer diffusivity isotherms of benzyl acetate in ethanol and α-tocopherol in carbon dioxide are graphed in Figures 8.a and 8.b, respectively. It is clear the good representations accomplished in both systems, and it may be detached this trend is common to the remaining systems. Actually, such findings are in accordance with the small average absolute deviation obtained (3.65%, Table 1).

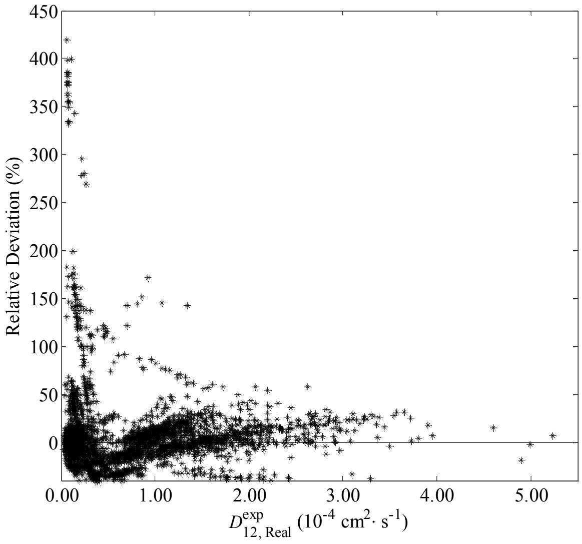

Figure 7. Relative deviations obtained with the Wilke-Chang model as function of experimental diffusivities.

Table 3. Average absolute relative deviations computed for two situations: (*i*) correlation of 90 systems with 2042 points totally; and (*ii*) prediction of those diffusivities using parameters estimated with the points at the highest temperatures.

Model	AARD (all data fitted)	AARD (partial fitting)
This Work	3.65	4.66
Dymond	4.90	9.20

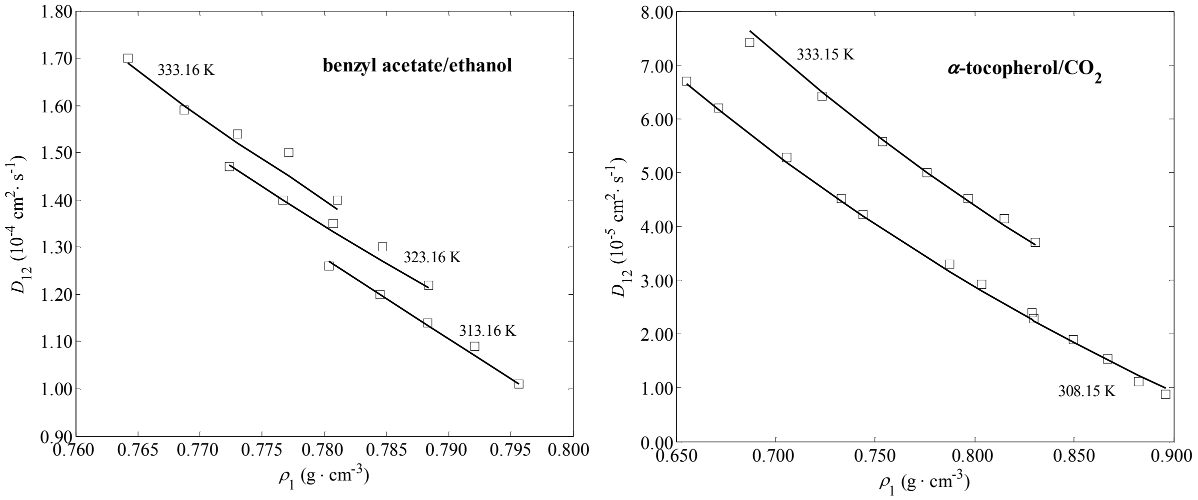

Figure 8. Tracer diffusion coefficients for the systems benzyl acetate/ethanol and α–tocopherol/carbon dioxide: experimental data and calculated results achieved with the new model.

4.PIV.6. Conclusions

In this work a new model for tracer diffusion coefficients of real polar and non-polar systems was proposed: Eq. (19) and subsidiary Eqs. (20) – (32). It is explicit and straightforward, and involves only two parameters (k_{12} and A_{12}). The required input data are temperature, number density of solvent, normal boiling point of solvent, molar volume at normal boiling point of solvent, and, for both components, the molecular weight, dipole moments, and LJ force constants (these are estimated as function of T_c and V_c).

The new model was validated with a large database containing 211 systems and 3463 experimental diffusivities, from which 141 systems and 1994 points refer to hydrogen-bonding solvents. All necessary properties for the 157 molecules involved in the database were collected and given in the Supplementary Data. The proposed model provided good and reliable results, giving rise to a global average absolute relative deviation of only 3.65%. Finally it must be emphasized its good prediction capability.

Nomenclature

A_{12}	binary parameter in the polar term
AARD	Average absolute relative deviation, $\mathrm{AARD} = \frac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left\| \left(D_{12,\mathrm{Real}}^{\mathrm{cacl}} - D_{12,\mathrm{Real}}^{\exp} \right) / D_{12,\mathrm{Real}}^{\exp} \right\|_i$, %
B	Parameter in Eq. (41)
D	Tracer diffusion coefficient, $\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
F	Correction factor of HS system
$\boldsymbol{F}$	Interaction force
$g(\sigma)$	Radial distribution function at contact
$G(k)$	Spatial Fourier transforms of $g(r)$
HS	Hard Sphere
k_B	Boltzmann constant, 1.380658×10^{-16} $\mathrm{erg} \cdot \mathrm{K}^{-1}$
k_{12}	Binary interaction parameter
LJ	Lennard-Jones
m	Mass of a molecule, g
M	Molecular weight, $\mathrm{g} \cdot \mathrm{mol}^{-1}$
NDP	Number of data points
NS	Number of systems
N_a	Avogadro constant, 6.0221367×10^{23} mol^{-1}
P	Pressure, bar
$\mathbf{P}$	Parachors
r	Radial coordinate, cm
T	Temperature, K
U	Intermolecular potential energy, J
$U^\mathrm{S}(k)$	Spatial Fourier transforms of $U^\mathrm{S}(r)$
V	Molar volume, $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
V_D	Parameter in Eq. (41), $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$

Greek letters

δ	Stockmayer parameter
η	Viscosity, cP

θ	Angle of inclination of the dipole axe
μ	Dipole moment, Debye
ζ	Friction coefficient
φ_1	HS packing fraction of solvent
ρ	Number density, N_a/V, cm^{-3}
ε	Attractive well depth
ε/k_B	Lennard-Jones energy parameter, K
σ	Molecular diameter, cm
ψ	Azimuthal angle

Subscripts

bp	Boiling point
BAH	Ben-Amotz and Herschbach
c	Critical property
eff	Effective hard sphere diameter (EHSD)
LJ	Lennard-Jones fluid
r	Reduced property
1, 11	Solvent
2	Solute
12	Binary property

Superscripts

0	Ideal gas
H	Hard sphere contribution
S,S	Soft attractive contribution
S,P	Polar term
*	Reduced quantity

Symbol

$\langle\ \rangle$	Average

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Paper V

Adapted from

Free-Volume Model for the Diffusion Coefficients of Solutes at Infinite Dilution in Supercritical CO_2 and Liquid H_2O

Journal of Supercritical Fluids, **2013**, 74, 89–104.

Abstract

A new free-volume model for tracer diffusion coefficients in supercritical CO_2 and liquid water is proposed in this work. It embodies the concepts of free volume and activation energy. The free volume is calculated by the Carnahan-Starling expression, and the necessary effective hard sphere diameter was taken from a previous publication. The model is explicit, straightforward, contains one parameter per system (activation energy), and only requires temperature, solvent density, solute molecular weight, and the solvent LJ constants. The validation of the model was accomplished with a large database, comprehending 289 systems with 5485 data points, and achieved only 3.56% of error. The fine predictive capability of the new expression was also demonstrated. The correlations of Wilke-Chang, Tyn-Calus, He-Yu-Su, Zhu *et al.*, and Dymond were adopted for comparison, but provided much poorer results and/or prediction values. A spreadsheet for the calculation of D_{12} is given in Supplementary Data.

3.PV.1. Introduction

The knowledge of diffusion coefficients and equilibrium data is essential for modeling processes involving mass transfer [1-2], such as separations and reactions. Particularly, the diffusion coefficients are important not only in chemical engineering calculations for design and simulation purposes, but also to extract information at microscopic level about the interaction between molecules [3].

Up till now, a considerable number of solubility data have been published, while diffusivities are still scarcer. Furthermore, most of the experimental binary diffusion coefficients at infinite dilution, D_{12}, found in the literature were measured in supercritical carbon dioxide (SC-CO_2) and liquid water, which reflects the interest and importance of these solvents.

The carbon dioxide, due to its low critical temperature ($T_c = 304.10\ \mathrm{K}$), moderate critical pressure ($P_c = 73.80\ \mathrm{bar}$), negligible surface tension, non-flammability, non--toxicity, etc., has been widely used, during last decades, as supercritical solvent or reaction medium. Despite being nonpolar, it is able to solubilize polar solutes at least at high densities, where the proximity between CO_2 and solute molecules is shortened, making possible interactions with its quadrupole that are almost absent at low densities. Moreover, the addition of small quantities of a polar cosolvent is generally sufficient to modify the solvent power and tune the selectivity of the supercritical solvent.

Aqueous solutions are the most common medium in research, industry, and nature. In contrast to carbon dioxide, the critical point of water is much higher ($T_c = 647.20\ \mathrm{K}$ and $P_c = 221.20\ \mathrm{bar}$), but supercritical and subcritical water have found interesting applications such as in catalytic gasification of biomass [4-5] and pressurized hot water extraction [6].

It is clear from the literature how the measured systems reflect their practical interest in terms of final applications. For instance, fatty acids, triacylglycerides, amino acids, sugars, and phenolic compounds have significant relevance in food, pharmaceutical, and fuel industries [2, 7-12]. Their presence in natural resources and the possibility to extract them with pure and modified SC-CO_2 or aqueous solutions, instead of organic solvents, increasingly requires their diffusivities in these solvents. Also worth mentioning are organometallic solutes in SC-CO_2, like palladium(II) acetylacetonate and cobalt(III) acetylacetonate, which have been largely used in the preparation and processing of advanced functional materials, as catalysts or precursors [13-14]. Other examples appear with the increasing interest of ionic liquids (ILs) [15] which is stressing their measurement in aqueous solution, because of the recovery step from water after processing [16].

In the whole, these examples clearly evidence the importance of tracer diffusivities in SC-CO_2 and liquid water for simulation and design. In fact, taking into account well known mixing rules (*e.g.*, Darken [17], Vignes [18], or others reviewed by Pertler *et al.* [19]) the diffusion coefficients in bulk mixtures can be then estimated and subsequently applied in multicomponent mass transfer calculations by means of the extended Fick's law or Maxwell-Stefan relationships [20-21]. Hence, the existence of D_{12} values of solutes in SC-CO_2 and liquid water is crucial, which requires the development of accurate models for their estimation since it is impossible to carry out experimental measurements for all systems and operating conditions. This is the main purpose of this work.

Several approaches for the calculation of diffusion coefficients in dense fluids can be found in the literature, such as the landmark Enskog theory [3, 22-23] for the hard sphere (HS) fluid and its modifications for real systems [3, 23], the effective hard sphere diameter method [23-26], the free-volume equations [23, 27-29], the van der Waals [23, 30-32] and rough hard sphere principles [23, 33-43], the hydrodynamic models based on Stokes-Einstein equation [44-45], the Eyring activated-state theory [46], and the excess entropy scaling laws [23, 47-49]. Most of these models and approaches are described and reviewed in detail by Reid *et al.* [44], Liong *et al.* [45], Silva and Liu [23], and Medina [50].

In this work, a new model for the tracer diffusion coefficients of solutes in supercritical carbon dioxide or liquid water is developed and then validated with a large database compiled from the literature. The model is a hybrid free-volume equation, where repulsive and attractive interactions are taken into account by the concepts of free volume and activation energy, respectively. The model embodies solvent parameters that were fitted to the whole database, and only one parameter that is system specific.

4.PV.2. Model Development

Molecules in a fluid composed of hard spheres move with the gas kinetic velocity, u , but part of the time stay confined into a cage bounded by their neighbors [27]. Furthermore, one may assumed the molecular transport results from the existence of: *i*) a molecular free volume higher than a critical value, v_{f}^{*}, which allows the particles to move between adjacent holes, and *ii*) an activation energy higher than a minimum value, ε^{*}, which allows the molecules to escape from the force field of its surroundings. In the case of a solute (2) diffusing through a solvent (1), both conditions must be satisfied in order to ensure both local free volume and energy for the transport [28, 51]. Then, the tracer diffusion coefficient, D_{12}, may be expressed as the product of that joint probability, p_{j}, by the solute velocity, *i.e.* $D_{12} \propto u_2 \, p_{\mathrm{j}}$. Here, $u_2 \propto \sqrt{T/M_2}$ is the gas kinetic velocity of the solute [3, 23], T is the absolute temperature, M_2 is the molecular weight of solute, and p_{j} is given by the original expression proposed by Macedo-Litovitz [28] and Chung [51]:

$$p_{\mathrm{j}} = \exp\left(-\frac{\gamma V_{\mathrm{f,1}}^{*}}{V_{\mathrm{f,1}}} - \frac{E_{\mathrm{a}}}{\Re_{\mathrm{g}} T} \right) \tag{1}$$

In Eq. (1), γ is a correction factor that takes into account the overlap of free volume and depends on each solvent, $V_{\mathrm{f,1}}^{*} = v_{\mathrm{f,1}}^{*} N_{\mathrm{a}}$ is the molar critical free volume of the solvent, N_{a} is the Avogadro's constant, $V_{\mathrm{f,1}}$ is the molar free volume of the solvent, $\Re_{\mathrm{g}}$ is the universal gas constant, and E_{a} is the activation energy (fitting parameter specific for each solvent/solute pair). The free volume is calculated here by the Carnahan-Starling equation of state [52] because it is very simple and represents accurately the HS fluid [23, 29, 52]:

$$\frac{V_{\mathrm{f,1}}}{V_1} = \exp\left[\frac{\varphi_1 (3\varphi_1 - 4)}{(1-\varphi_1)^2} \right] \tag{2}$$

where V_1 is the molar volume of the solvent, and $\varphi_1 = \frac{N_{\mathrm{a}} \pi \sigma_1^3}{6 V_1} = \frac{\pi}{6} \rho_1 \sigma_1^3 = \frac{\pi}{6} \rho_1^{*}$ is the HS packing fraction of the solvent; ρ_1 is the number density of the solvent, σ_1 is its molecular diameter, and $\rho_1^{*} \equiv \rho_1 \sigma_1^3$ is the well-known reduced density of solvent.

An effective hard sphere diameter, $\sigma_{\mathrm{eff,1}}$, will be used instead of σ_1 to capture the softness of the repulsive interactions between the real solvent molecules. The expression utilized in this work was derived by Silva *et al.* [26] on the basis of the Boltzmann criterion, which approximates $\sigma_{\mathrm{eff,1}}$ by the distance of closest approach of a colliding pair of molecules with the average relative kinetic energy, subjected to soft repulsive interactions. Its good behavior was tested and evidenced by Liu *et al.* [23, 26].

$$\sigma_{\mathrm{eff,1}} = \sigma_{\mathrm{LJ,1}} \times 2^{1/6} \left[1 + \left(1.3229 T_1^{*} \right)^{1/2} \right]^{-1/6} \tag{3}$$

$$T_1^{*} \equiv \frac{k_{\mathrm{B}} T}{\varepsilon_{\mathrm{LJ,1}}} \tag{4}$$

where $\sigma_{\mathrm{LJ,1}}$ and $\varepsilon_{\mathrm{LJ,1}}$ are the solvent Lennard-Jones (LJ) force constants, T_1^{*}, is the reduced temperature of the solvent, and k_{B} is the Boltzmann's constant. For carbon dioxide, the LJ parameters were taken from Table 7 of Liu *et al.* [33], and for water they were taken from Reid *et al.* [44]. The values for both solvents are listed in Table 1.

The final expression proposed in this work for the tracer diffusion coefficients of real systems, $D_{12,\,\mathrm{Real}}$, is given by:

$$D_{12,\,\mathrm{Real}} = \frac{A}{\rho_1^{*0.5}} \sqrt{\frac{T}{M_2}} \exp\left(-\frac{\gamma V_1^*}{V_{\mathrm{f},1}} - \frac{E_\mathrm{a}}{\Re_\mathrm{g}\, T} \right) \tag{5}$$

where A is a proportionality constant. Since parameters $\gamma V_{\mathrm{f},1}^*$ and A are intimately related with the solvent, they should be fitted to the entire database of $D_{12,\,\mathrm{Real}}$ values compiled in this essay. The remaining parameter is the system-specific activation energy, E_a. Its values can be optimized using the individual sets of experimental data for each solvent/solute pair. Finally, Eq. (5) embodies the simple density correction $\rho_1^{*0.5}$ in the denominator of its right hand side in order to extend its applicability to the entire range of supercritical state, where a biased behavior would be observed otherwise. For liquid water it has no impact since its density is essentially constant. This correction could be also accomplished using the free volume, but the final model would get more complex without improving the results.

Table 1. Parameters of the new model (Eqs. (5) + (2) – (4)) and LJ force constants for both carbon dioxide [33] and water [44].

Solvent	$A \times 10^4$ $(\mathrm{cm}^2 \cdot \mathrm{g}^{0.5} \cdot \mathrm{s}^{-1} \cdot \mathrm{mol}^{-0.5} \cdot \mathrm{K}^{-0.5})$	γV_1^* $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$\sigma_{\mathrm{LJ},1}$ (Å)	$\varepsilon_{\mathrm{LJ},1}/k_\mathrm{B}$ (K)
Supercritical CO_2	1.035	7.895	3.26192	500.71
Liquid H_2O	35.40	1.000	2.64100	809.1

4.PV.3. Models Adopted for Comparison

In this work five tracer diffusivity models were adopted for comparison. With zero parameters, the hydrodynamic expressions of Wilke-Chang (WC) [44-45, 53] and Tyn-Calus (TC) [44-45, 54], and the equations of Zhu *et al.* (Zhu) [55] and He-Yu-Su (HYS) [56]. With two parameters, the correlation of Dymond (DHB) [23, 30]. In the following, their expressions are briefly presented.

4.PV.3.1. ***Wilke-Chang Equation*** (WC) [44-45, 53]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=7.4\times10^{-8}\,\frac{T\sqrt{\phi_1 M_1}}{\eta_1 V_{\mathrm{bp},2}^{0.6}} \tag{6}$$

ϕ_1 is a dimensionless association factor of the solvent (for carbon dioxide $\phi_1 = 1$, and for water $\phi_1 = 2.26$ [57]), M_1 is the solvent molecular weight in $\mathrm{g\cdot mol^{-1}}$, η_1 is the solvent viscosity in cP, and $V_{\mathrm{bp},2}$ is the solute molar volume at normal boiling point in $\mathrm{cm^3\cdot mol^{-1}}$.

4.PV.3.2. ***Tyn-Calus Equation*** (TC) [44-45, 54]

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\left(\frac{V_{\mathrm{bp},2}}{V_{\mathrm{bp},1}^{2}}\right)^{1/6}\left(\frac{\mathbf{P_1}}{\mathbf{P_2}}\right)^{0.6}\frac{T}{\eta_1} \tag{7}$$

$\mathbf{P}$ identifies parachors, which are related to the liquid surface tension and may be estimated by additive group contributions, giving rise to:

$$D_{12}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\,\frac{V_{\mathrm{bp},1}^{0.267}}{V_{\mathrm{bp},2}^{0.433}}\,\frac{T}{\eta_1} \tag{8}$$

4.PV.3.3. ***Model of Zhu et al.*** (Zhu) [55]

This model was developed for the LJ fluid and extended to real systems. The repulsive interactions were introduced using the HS expression of Speedy [23, 58], and the attractive contribution was represented by an exponential term. This equation is applicable to gas, liquid, and supercritical systems where the solvent is nonpolar or weakly polar:

$$\begin{aligned} D_{12} = {} & \frac{3}{8\sqrt{\pi}}\sqrt{\frac{\sigma_{\mathrm{LJ},12}^{2}\,\varepsilon_{\mathrm{LJ},12}}{m_1}}\,\frac{\sqrt{T_{12}^{*}}}{\rho_{12}^{*}}\left(1-\frac{\rho_{12}^{*}}{1.029079\,T_{12}^{*\,0.165377}}\right)\\ & \times\left[1+\rho_{12}^{*\,0.126978}\left(\frac{0.596103\left(\rho_{12}^{*}-1\right)}{0.539292\left(\rho_{12}^{*}-1\right)+T_{12}^{*\left(0.400152-0.41054\rho_{12}^{*}\right)}}+0.68856\right)\right]\\ & \times\exp\left(-\frac{\rho_{12}^{*}}{2\,T_{12}^{*}}\right) \end{aligned} \tag{9}$$

Here, m_1 is the mass of the solvent molecule, and T_{12}^{*} and ρ_{12}^{*} are the reduced temperature and density computed using the combined LJ energy and diameter:

$$T_{12}^{*}=\frac{T}{\varepsilon_{\mathrm{LJ},12}/k_{\mathrm{B}}} \quad \text{and} \quad \rho_{12}^{*}=\rho_{1}\,\sigma_{\mathrm{LJ},12}^{3} \tag{10}$$

The combining rules adopted to compute binary parameters are:

$$\begin{gathered}\varepsilon_{\mathrm{LJ},12}/k_{\mathrm{B}}=\sqrt{\left(\varepsilon_{\mathrm{LJ},1}/k_{\mathrm{B}}\right)\times\left(\varepsilon_{\mathrm{LJ},2}/k_{\mathrm{B}}\right)}\\ \sigma_{\mathrm{LJ},12}=\left(1-k_{12}^{\mathrm{d}}\right)\frac{\sigma_{\mathrm{LJ},1}+\sigma_{\mathrm{LJ},2}}{2}\;, \qquad \text{where } k_{12}^{\mathrm{d}}=0.7926\frac{\sigma_{\mathrm{LJ},2}-\sigma_{\mathrm{LJ},1}}{\sigma_{\mathrm{LJ},1}+\sigma_{\mathrm{LJ},2}}\end{gathered} \tag{11}$$

The LJ parameters of the solvent and solute are estimated by distinct expressions:

$$\varepsilon_{\mathrm{LJ},1}/k_{\mathrm{B}}=\frac{T_{\mathrm{c},1}}{T_{\mathrm{c},1}^{*}}\left[1+0.47527332\,\rho_{\mathrm{r},1}+\left(0.06300484+0.12374707\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{12}$$

$$\sigma_{\mathrm{LJ},1}=\left(\frac{\rho_{\mathrm{c},1}^{*}}{\rho_{\mathrm{c},1}}\right)^{1/3}\left[1-0.0368868\rho_{\mathrm{r},1}+\left(0.00006945+0.01089228\rho_{\mathrm{r},1}\right)T_{\mathrm{r},1}\right] \tag{13}$$

$$\varepsilon_{\mathrm{LJ},2}/k_{\mathrm{B}}=\frac{T_{\mathrm{c},2}}{1.313} \quad \text{and} \quad \sigma_{\mathrm{LJ},2}=\sqrt[3]{\frac{0.13\;\varepsilon_{\mathrm{LJ},2}}{P_{\mathrm{c},2}}} \tag{14}$$

where subscript ‘c’ denotes critical property, and ‘r’ reduced property (reduction performed with critical constants). The expressions given in Eq. (16) are based on the principle of corresponding states and on the critical point computed by Johnson *et al.* [59], which for the LJ fluid is $P_{\mathrm{c}}^{*}=0.13$, $T_{\mathrm{c}}^{*}=1.313$, and $\rho_{\mathrm{c}}^{*}=0.31$.

4.PV.3.4. He-Yu-Su correlation (HYS) [56]

This equation is specific for supercritical systems:

$$\begin{gathered}D_{12}\left(\mathrm{cm}^{2}\cdot\mathrm{s}^{-1}\right)=A'\times10^{-7}\left(V_{1}^{k}-B'\right)T/\sqrt{M_{2}}\\ k=1,\quad \rho_{\mathrm{r},1}\geq1.2\\ k=1+\left(\rho_{\mathrm{r},1}-1.2\right)/\sqrt{M_{1}}\,,\quad \rho_{\mathrm{r},1}<1.2\end{gathered} \tag{15}$$

V_1 is the solvent molar volume in $\mathrm{cm^3 \cdot mol^{-1}}$, and parameters A' and B' depend only on the solvent properties (molecular weight, and critical volume, pressure and temperature):

$$A' = 0.29263 + 1.6736 \exp\left(-0.75832 \sqrt{M_1 V_{\mathrm{c},1}} \big/ P_{\mathrm{c},1}\right), \quad \rho_{\mathrm{r},1} \geq 0.21$$
$$B' = 0.077\, T_{\mathrm{c},1}, \quad \rho_{\mathrm{r},1} \geq 0.21 \tag{16}$$

4.PV.3.5. Dymond Free-Volume expression (DHB) [23, 30]

This model embodies two adjustable parameters: B is a constant characteristic of the solvent-solute pair, and V_D is a constant related primarily with the solvent. We use DHB as acronym since this equations should be correctly attributed to Dymond [30], Hildebrand [60], and Batschinski [61].

$$D_{12} = B\sqrt{T}\left(V_1 - V_\mathrm{D}\right) \tag{17}$$

4.PV.4. Model Validation: Database and Data for Calculations

It is worth noting the increasing number of publications containing experimental data in last decades, which confirms the growing interest on green separation and reaction techniques. In this work a large database of tracer diffusion coefficients in supercritical carbon dioxide and liquid water has been compiled: 289 binary systems performing 5485 points (166 systems/4323 points in supercritical CO_2, and 124 systems/1162 points in liquid H_2O). Table 3.1 (Chapter 3) contains all systems studied, the reduced ranges of temperature, pressure, and density (reduction performed with critical constants), the number of data points (NDP), and the data sources for each system. Some authors do not report the densities and viscosities of carbon dioxide and water, and in these cases those values were calculated by different correlations found in the literature. For carbon dioxide, they were calculated by Pitzer and Schreiber [62] and Altunin and Sakhabetdinov [63] correlations, respectively, and for water the same properties were estimated by IAPWS [64]. The unknown molar volumes at normal boiling point were estimated by Tyn-Calus [65] equation, and the unknown critical constants were predicted by different methods (*e.g.*, Joback [44, 66-67], Ambrose [44, 68-69], Klincewicz [44, 70], Wen and Qiang [71]). For ionic liquids, the critical constants were taken from

Valderrama and Rojas [72]. As much as possible, all diffusivity data available in the literature were used, though data provided in graphical form have been rejected.

4.PV.5. Results and Discussion

The model proposed in this work (Eq. (5) + subsidiary Eqs. (2) – (4)) is straightforward and simple to use, and the necessary input data are temperature (K), solvent number density (cm^{-3}), the molecular weight of the solute ($\mathrm{g\cdot mol^{-1}}$), and the activation energy, E_a ($\mathrm{erg\cdot mol^{-1}}$), that is the unique parameter of the system. A spreadsheet for the calculation of D_{12} is given in Supplementary Data, where readers are requested to provide the name of the solute, and the conditions of temperature (K) and solvent density (for simplicity, it is given the opportunity to insert it in $\mathrm{g\cdot cm^{-3}}$).

The model parameters of the solvent are the LJ diameter and energy ($\sigma_{\mathrm{LJ},1}$ and $\varepsilon_{\mathrm{LJ},1}/k_\mathrm{B}$), and constants $\gamma V_{\mathrm{f},1}^{*}$ and A. These two values were optimized for both solvents using the whole database; their values are listed in Table 1.

Table 2 contains a detailed compilation of the results obtained with the new model (Eqs. (5) + (2) – (4)), and the other equations adopted for comparison: WC, TC, Zhu, HYS, DHB. The global results per solvent and the grand averages are presented in Table 3.

From Table 2 it is possible to observe the reliability and the accuracy of our model for both type of solvents – supercritical carbon dioxide and liquid water – since it provides systematically low average absolute relative deviations (AARDs) in the range 0.59 – 13.45%.

It may be emphasized the good performance achieved for the aqueous systems whose solutes are ionic liquids: [Bmim][BF_4], [Bmim][bti], [Bmim][CF_3SO_3], [Bmim][Cl], [Bmim][$MeSO_4$], [Bmim][$OcSO_4$], [Bmim][PF_6], [Emim][BF_4], [Emim][bti], [Emim][$C_2H_5SO_4$], [Emim][C_2N_3], [Emim][CF_3SO_3], [Emim][$MDEGSO_4$], [Hmim][bti], and [Omim][bti]. In all cases, the relative deviations are less than 5.5%. Furthermore, it is interesting to note that our database include 18 systems with points for liquid CO_2.

Table 2. Calculated results: average deviations, parameters of the models, and number of data points.

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	acetone	178	1.21634	4.18	2.1316	13.74	5.05	5.64	5.48	4.15	11.71
carbon dioxide	acridine	6	1.35267	2.63	1.2634	16.55	2.85	4.93	12.06	3.50	15.47
carbon dioxide	adamantanone	8	0.24222	2.06	1.4379	-2.78	2.59	18.17	13.45	31.54	29.47
carbon dioxide	allylbenzene	15	1.38883	2.51	1.3060	10.81	3.34	5.36	8.42	4.39	10.60
carbon dioxide	aniline	15	1.92647	2.83	1.1791	8.61	2.46	33.34	33.91	25.07	21.45
carbon dioxide	anisole	15	1.41445	1.89	1.4822	13.90	2.97	7.33	11.77	3.35	7.70
carbon dioxide	anthracene	22	1.10404	5.97	1.6433	22.35	1.75	10.38	2.86	10.72	20.69
carbon dioxide	arachidonic acid (AA)	75	1.46431	1.90	0.8591	13.44	2.51	9.70	16.13	7.61	49.72
carbon dioxide	AA ethyl ester	48	1.25637	4.73	1.1233	23.26	1.17	15.16	10.26	1.53	37.41
carbon dioxide	behenic acid ethyl ester	17	1.24949	4.61	1.2263	27.32	0.86	21.34	5.03	2.73	65.88
carbon dioxide	benzene	222	0.94500	6.21	1.4921	-1.03	7.59	9.14	9.23	10.21	11.77
carbon dioxide	benzoic acid	29	1.17011	5.65	1.8170	21.69	6.34	9.27	13.02	6.05	8.54
carbon dioxide	benzyl acetate	15	1.41509	1.89	1.3600	16.99	3.02	7.79	17.75	3.24	9.82
carbon dioxide	benzylacetone	15	1.53598	1.83	1.0795	9.68	3.76	6.19	17.90	9.19	12.63
carbon dioxide	biphenyl	24	1.05895	3.07	1.3557	13.85	3.39	10.13	6.94	8.45	15.21
carbon dioxide	2-bromoanisole	15	1.01736	1.87	1.2561	12.79	3.66	16.52	23.81	11.27	10.23
carbon dioxide	bromobenzene	15	0.95738	3.93	1.4373	12.25	4.36	7.81	10.55	14.21	9.08
carbon dioxide	2-butanone	38	1.23424	1.53	2.0672	16.91	2.60	5.38	5.39	3.98	9.83
carbon dioxide	*n*-butylbenzene	15	1.38269	0.94	1.4109	15.95	2.97	6.29	5.39	2.77	11.18
carbon dioxide	*tert*-butylbenzene	15	1.29234	3.11	1.8018	23.59	3.62	7.92	3.35	3.26	9.25

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	1.38211	1.30	1.5998	22.80	3.10	8.49	5.79	3.32	13.66
carbon dioxide	butyric acid ethyl ester	16	1.22795	4.31	2.2177	27.36	1.89	4.31	2.96	3.54	3.91
carbon dioxide	caffeine	21	1.23011	3.79	0.7164	-17.53	4.87	22.62	36.24	6.83	37.00
carbon dioxide	capric acid ethyl ester	16	1.24040	4.51	1.7729	29.09	1.44	13.46	3.77	2.88	10.56
carbon dioxide	caprylic acid ethyl ester	16	1.24972	3.61	1.7619	26.83	1.67	10.23	4.14	2.45	7.39
carbon dioxide	β-carotene	90	1.54903	1.31	0.6748	16.79	2.26	14.88	20.36	8.79	144.58
carbon dioxide	L-carvone	27	1.40627	3.37	1.6464	23.91	2.62	3.66	12.00	4.76	10.97
carbon dioxide	chlorobenzene	15	1.30122	3.27	1.4476	11.52	3.61	8.22	10.29	5.24	8.91
carbon dioxide	chrysene	4	0.99232	1.36	1.8594	27.80	2.61	16.16	2.80	13.69	43.90
carbon dioxide	citral	15	1.24382	4.55	1.3860	16.29	4.31	8.63	5.29	3.50	10.55
carbon dioxide	cobalt(III) acetylacetonate	38	0.92648	1.48	1.0715	17.87	2.13	11.53	29.97	12.44	125.95
carbon dioxide	copper(II) trifluoroacetylacetonate	12	0.71621	4.85	1.2764	22.66	5.04	37.09	49.65	17.87	72.60
carbon dioxide	15-crown-5	29	0.84574	2.56	0.9986	1.19	5.98	7.85	12.64	13.43	21.17
carbon dioxide	cycloheptanone	8	1.38537	3.69	1.8569	23.71	1.85	24.01	26.38	5.33	8.58
carbon dioxide	cyclononanone	8	1.34189	3.94	1.7583	25.46	2.33	17.62	25.13	4.12	10.68
carbon dioxide	cyclopentanone	8	1.41788	1.88	1.8382	18.40	1.03	20.31	19.56	7.64	13.18
carbon dioxide	*n*-decane	5	0.56607	3.87	3.8443	36.48	1.47	38.51	29.10	27.51	32.31
carbon dioxide	dibenzo-24-crown-8	28	1.10446	1.24	1.0944	24.24	1.93	12.73	13.08	9.04	99.02
carbon dioxide	dibenzyl ether	15	1.44889	1.43	1.0702	14.04	3.22	5.32	20.72	5.56	15.81
carbon dioxide	1,2-dichlorobenzene	15	1.08073	2.13	1.5427	16.61	2.07	6.89	11.69	9.25	10.51

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	1,3-dichlorobenzene	4	1.20913	3.19	2.4973	31.57	1.11	11.52	16.96	6.42	2.48
carbon dioxide	*p*-dichlorobenzene	13	1.03563	3.54	1.5067	16.27	3.72	10.61	16.00	8.46	8.76
carbon dioxide	diethyl ether	15	1.27343	4.80	1.0474	-26.59	4.98	11.80	12.38	6.98	32.29
carbon dioxide	1,2-diethylbenzene	15	1.40057	1.34	1.3663	15.06	2.61	6.19	6.01	3.30	11.78
carbon dioxide	1,4-diethylbenzene	15	1.40413	1.66	1.3865	15.72	4.06	5.65	6.72	3.56	11.17
carbon dioxide	diisopropyl ether	15	1.07447	6.16	1.0782	-16.29	7.87	7.14	6.46	8.47	29.92
carbon dioxide	2,4-dimethyl-3-pentanone	8	1.61018	3.94	1.7583	25.46	2.33	11.25	20.20	15.38	24.76
carbon dioxide	2,3-dimethylaniline	15	1.75043	2.43	1.2259	13.77	2.38	16.04	24.54	16.97	12.08
carbon dioxide	2,6-dimethylaniline	15	1.59383	2.66	1.1330	8.66	3.34	11.47	19.64	12.35	11.78
carbon dioxide	1,1'-dimethylferrocene	68	0.72103	1.97	1.2835	11.85	3.67	12.16	20.35	17.13	29.12
carbon dioxide	2,3-dimethylnaphthalene	3	1.29192	1.57	1.5361	21.43	1.08	3.66	8.29	1.25	10.35
carbon dioxide	2,6-dimethylnaphthalene	6	1.26237	3.42	1.1736	10.78	4.24	7.15	9.26	5.28	15.38
carbon dioxide	2,7-dimethylnaphthalene	6	1.32293	4.34	1.5069	19.63	4.50	6.91	6.00	4.68	11.91
carbon dioxide	2,4-dimethylphenol	15	1.52518	2.87	1.1649	8.33	3.63	9.42	16.90	8.03	11.95
carbon dioxide	diolein	9	1.16202	0.89	0.6769	14.02	1.61	23.69	9.91	4.84	77.97
carbon dioxide	1,3-divinylbenzene	15	1.34191	1.52	1.5589	18.35	1.39	3.74	7.74	2.34	12.10
carbon dioxide	docosahexaenoic acid (DHA)	63	1.51655	0.99	0.9162	18.60	1.63	7.28	19.86	9.19	58.53
carbon dioxide	DHA ethyl ester	65	1.24028	4.31	1.0708	22.09	1.45	16.73	9.27	1.67	48.46
carbon dioxide	DHA methyl ester	17	1.24147	3.94	1.2079	25.70	0.92	16.76	8.37	2.34	52.38
carbon dioxide	*n*-dodecane	5	0.54103	5.65	4.3507	39.93	2.99	40.87	29.79	29.20	37.54

Table 2 (Continued)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	eicosapentaenoic acid (EPA)	55	1.45080	1.25	0.9184	16.15	1.79	7.79	17.55	7.35	46.01
carbon dioxide	EPA ethyl ester	48	1.25376	5.08	1.1626	24.23	1.06	14.98	10.14	1.55	36.48
carbon dioxide	EPA methyl ester	17	1.29580	4.58	1.2964	27.43	0.49	17.37	7.27	1.65	37.76
carbon dioxide	ethanol	24	1.34433	2.25	1.9621	6.43	3.21	11.29	5.39	4.48	12.41
carbon dioxide	ethyl acetate	15	1.17624	7.36	0.8254	-49.61	6.71	12.75	13.77	8.62	36.32
carbon dioxide	ethyl benzoate	15	1.46985	4.53	1.8993	27.23	2.94	3.88	12.77	4.95	12.20
carbon dioxide	ethylbenzene	15	1.21923	1.39	1.8248	18.85	2.28	7.44	3.41	4.72	9.47
carbon dioxide	2-ethyltoluene	15	1.45292	2.23	1.4172	14.72	3.76	8.95	4.63	5.62	9.30
carbon dioxide	3-ethyltoluene	15	1.46560	2.59	1.4175	14.91	4.00	11.68	5.28	6.07	9.82
carbon dioxide	4-ethyltoluene	15	1.52918	2.05	1.4780	17.40	3.07	7.46	4.10	8.12	8.89
carbon dioxide	eugenol	15	1.55817	2.10	1.3885	20.62	3.58	17.29	28.35	7.33	10.54
carbon dioxide	ferrocene	107	0.69620	2.86	1.2243	5.68	6.96	17.43	21.04	19.84	21.29
carbon dioxide	2-fluoroanisole	15	1.35210	1.74	1.3944	14.19	2.58	18.48	22.85	3.35	9.93
carbon dioxide	fluorobenzene	15	1.35066	3.04	1.7808	17.76	4.22	11.04	11.16	4.34	10.40
carbon dioxide	3-fluorophenol	4	1.55335	3.27	2.5285	31.70	1.00	13.15	17.99	6.50	15.67
carbon dioxide	geraniol	4	1.77497	3.33	2.0523	32.28	0.38	3.34	18.04	15.01	3.39
carbon dioxide	*n*-heptane	5	0.82119	3.40	3.9421	35.67	1.00	28.91	22.68	19.03	20.99
carbon dioxide	2-heptanone	11	0.51719	5.20	3.4792	32.29	1.83	30.11	24.33	26.86	22.02
carbon dioxide	4-heptanone	9	0.28500	2.92	3.1752	27.31	0.47	36.53	30.93	32.43	29.62
carbon dioxide	hexachlorobenzene	14	0.41353	3.38	0.8331	-12.47	4.18	10.99	13.01	25.68	25.04

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3 · mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	1-hexadecene	11	1.42110	7.73	0.7329	-8.63	11.75	16.17	11.89	10.01	35.05
carbon dioxide	1,1,1,5,5,5-hexafluoroacetylacetone	15	0.99453	3.25	1.1460	11.05	4.36	18.95	27.98	10.10	23.39
carbon dioxide	*n*-hexane	5	0.99320	2.94	3.9838	35.55	2.09	22.91	18.40	14.11	16.06
carbon dioxide	iodobenzene	15	0.83131	2.60	1.2680	11.18	2.72	12.21	17.69	16.88	11.69
carbon dioxide	D-limonene	15	1.25046	3.27	1.3735	12.04	4.06	9.32	4.27	4.03	10.49
carbon dioxide	linalool	15	1.22120	3.90	1.3508	14.09	4.02	7.24	5.63	3.52	11.26
carbon dioxide	linoleic acid	71	1.42115	1.88	0.8351	9.74	3.73	9.63	15.88	7.14	30.68
carbon dioxide	linoleic acid methyl ester	21	1.36205	1.94	1.0645	19.77	1.66	15.74	7.44	2.11	56.92
carbon dioxide	α-linolenic acid	56	1.39441	1.34	0.9745	15.74	2.79	14.24	9.32	5.15	26.31
carbon dioxide	γ-linolenic acid	142	1.44530	1.83	0.8364	9.15	2.15	7.79	16.90	7.90	33.37
carbon dioxide	γ-linolenic acid ethyl ester	41	1.04236	5.94	0.8603	6.15	5.10	6.92	27.87	9.79	43.72
carbon dioxide	γ-linolenic acid methyl ester	52	1.05880	7.05	0.8588	7.53	7.58	13.41	10.20	6.85	47.11
carbon dioxide	L-menthone	23	1.31302	4.01	1.7676	25.22	2.81	5.18	7.36	3.65	11.73
carbon dioxide	methanol	10	1.29728	1.95	2.1980	1.60	2.14	16.79	7.10	6.17	20.87
carbon dioxide	*N*-(4-methoxybenzylidene)-4-*n*-butylaniline	5	0.35550	1.98	2.1419	29.00	0.33	17.85	5.56	30.23	42.04
carbon dioxide	methyl orange	60	0.47888	4.39	1.4242	20.75	4.13	-	-	28.32	-
carbon dioxide	2-methylanisole	15	1.44329	1.78	1.3055	12.12	2.79	9.67	16.19	5.18	9.69
carbon dioxide	4-methylanisole	15	1.64350	1.43	1.3473	16.11	3.21	17.52	24.50	12.63	12.16
carbon dioxide	1-methylnaphthalene	11	1.70451	5.70	0.7415	-17.13	6.64	20.35	30.86	19.06	37.94
carbon dioxide	monoolein	11	1.37004	0.59	0.8199	13.88	1.22	8.71	18.90	5.13	24.17

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	myristic acid ethyl ester	16	1.22681	4.53	1.4546	27.11	2.14	15.97	4.92	3.07	24.88
carbon dioxide	myristoleic acid	42	1.50760	1.15	0.8465	4.77	2.66	5.68	22.90	13.91	25.97
carbon dioxide	myristoleic acid methyl ester	79	1.11760	9.35	0.7247	-15.38	10.07	10.41	19.80	11.93	68.29
carbon dioxide	naphthalene	112	0.98691	8.08	1.1749	0.32	9.86	10.87	10.33	11.49	19.36
carbon dioxide	1-naphthol	11	0.73194	3.93	2.1460	24.53	0.88	5.77	0.39	18.59	9.22
carbon dioxide	2-naphthol	16	0.65533	9.15	1.9948	21.27	1.73	7.84	2.46	23.33	6.52
carbon dioxide	2-nitroanisole	15	1.40360	1.38	1.2984	15.75	2.39	11.47	20.75	3.48	10.88
carbon dioxide	nitrobenzene	15	1.28768	1.95	1.2975	9.79	3.33	8.79	13.98	4.21	9.96
carbon dioxide	3-nitrotoluene	15	1.31463	1.79	1.3849	14.90	3.96	4.00	8.67	2.86	9.58
carbon dioxide	*n*-nonane	5	0.63938	3.82	4.0604	37.02	1.43	36.45	27.94	25.69	29.33
carbon dioxide	2-nonanone	10	0.32573	5.59	2.8331	29.00	2.35	35.76	27.22	29.36	25.05
carbon dioxide	5-nonanone	12	0.52082	5.95	3.0575	32.15	1.10	34.31	25.24	26.31	25.83
carbon dioxide	*n*-octane	5	0.73943	3.76	4.1527	37.05	1.66	33.41	25.91	22.91	25.60
carbon dioxide	oleic acid	19	1.43688	1.14	0.8088	9.94	2.14	10.03	16.61	7.78	37.36
carbon dioxide	oleic acid ethyl ester	5	1.29836	2.46	0.5458	-23.03	0.97	5.72	27.68	5.13	53.72
carbon dioxide	oleic acid methyl ester	19	1.28264	2.39	0.5031	-34.23	1.93	6.50	31.10	6.26	65.15
carbon dioxide	paladium(II) acetylacetonate	125	0.71368	2.83	1.2460	17.11	4.65	21.93	32.80	18.95	91.51
carbon dioxide	palmitic acid ethyl ester	17	1.31427	4.14	1.3142	26.47	0.61	15.14	8.02	1.46	30.82
carbon dioxide	*n*-pentane	5	1.21416	3.10	4.0586	35.82	1.67	13.23	11.26	6.62	9.12
carbon dioxide	2-pentanone	23	1.20772	1.33	1.7185	12.62	2.52	4.45	4.27	4.35	7.78

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
carbon dioxide	3-pentanone	39	1.19670	1.22	2.0419	19.27	2.03	9.48	6.20	4.22	9.03
carbon dioxide	*n*-pentylbenzene	31	1.39860	1.33	1.6182	21.86	3.86	8.38	5.24	3.85	12.91
carbon dioxide	phenanthrene	19	0.91424	5.00	1.3448	12.04	5.03	13.96	7.78	13.72	23.94
carbon dioxide	phenol	109	1.17968	2.51	1.3527	2.15	4.66	21.20	17.97	5.30	7.84
carbon dioxide	2-phenyl-1-propanol	15	1.56311	1.43	1.2825	15.24	2.64	9.72	19.88	9.53	15.83
carbon dioxide	3-phenyl-1-propanol	15	1.53772	1.66	1.5158	20.64	2.28	6.21	16.54	7.82	9.50
carbon dioxide	phenylacetic acid	16	1.33119	2.57	1.7122	22.71	1.80	4.25	12.95	1.62	6.41
carbon dioxide	phenylacetylene	15	1.43101	1.30	1.6377	17.26	1.58	7.80	12.00	4.46	7.61
carbon dioxide	1-phenyldodecane	15	1.71696	1.63	0.9485	17.21	3.14	6.96	18.09	16.09	26.54
carbon dioxide	1-phenylethanol	15	1.51442	1.48	1.3428	14.22	3.15	10.31	17.97	7.66	11.15
carbon dioxide	2-phenylethanol	15	1.52751	1.16	1.3652	15.18	3.03	12.10	19.59	8.49	10.31
carbon dioxide	2-phenylethyl acetate	15	1.56862	1.62	1.1080	13.22	3.06	8.63	22.22	9.82	13.89
carbon dioxide	1-phenylhexane	15	1.43036	1.55	1.2534	16.08	2.71	7.52	7.80	4.98	14.59
carbon dioxide	phenylmethanol	15	1.49672	1.44	1.5257	16.57	2.54	13.91	18.50	7.02	8.05
carbon dioxide	1-phenyloctane	15	1.41001	1.63	1.1894	16.53	3.65	8.65	8.49	3.77	20.79
carbon dioxide	3-phenylpropyl acetate	15	1.58569	2.64	1.0565	12.96	3.37	7.12	21.63	9.79	14.86
carbon dioxide	α-pinene	15	1.24350	5.18	1.7055	21.73	3.83	7.00	4.66	4.11	9.38
carbon dioxide	β-pinene	15	1.09790	3.25	1.3716	9.22	4.97	11.72	4.07	6.66	10.14
carbon dioxide	1-propanol	17	1.36432	3.42	1.3448	-10.04	3.00	15.43	11.60	10.36	8.71
carbon dioxide	2-propanol	18	1.29100	1.86	1.5735	-1.37	2.21	9.57	6.96	6.43	7.42

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ ($erg \cdot mol^{-1}$)	AARD	$B \times 10^{7}$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*i*-propylbenzene	15	1.21239	1.83	1.6274	17.00	2.00	9.27	4.11	4.82	10.94
carbon dioxide	*n*-propylbenzene	34	1.31027	4.71	0.8647	-17.49	5.03	12.75	14.62	8.65	25.18
carbon dioxide	pyrene	18	1.21328	5.09	1.5497	23.47	1.84	9.18	5.95	6.84	26.23
carbon dioxide	squalene	5	1.01454	4.92	1.9069	36.68	1.87	13.56	11.21	10.81	50.04
carbon dioxide	stearic acid ethyl ester	17	1.30430	4.39	1.2474	26.37	1.03	16.25	8.48	1.65	41.53
carbon dioxide	styrene	15	1.57318	3.38	1.6454	18.93	4.39	5.38	9.91	9.17	8.35
carbon dioxide	*n*-tetradecane	5	0.59123	7.94	4.3703	41.99	3.32	38.78	25.35	25.26	43.05
carbon dioxide	tetrahydrofuran	15	1.14634	5.43	1.1871	-22.18	4.99	15.96	12.43	8.80	22.16
carbon dioxide	2,2,4,4-tetramethyl-3-pentanone	9	0.24859	3.68	3.0352	29.08	0.76	27.01	21.41	33.00	24.62
carbon dioxide	thenoyltrifluoroacetone	15	1.29605	3.46	1.1938	18.09	3.05	30.20	41.38	4.04	13.70
carbon dioxide	a-tocopherol	82	1.04578	1.22	0.9419	18.16	2.21	31.55	5.63	9.43	64.17
carbon dioxide	toluene	35	1.18363	3.71	1.6490	11.46	4.14	5.32	5.03	5.43	8.44
carbon dioxide	triarachidonin	27	1.01312	3.21	0.4912	6.85	0.82	17.49	20.63	10.98	149.21
carbon dioxide	trierucin	101	1.20590	3.69	0.3731	-2.73	2.95	13.57	31.19	7.37	146.62
carbon dioxide	trifluoroacetylacetone	15	0.91159	2.06	1.7229	19.57	2.18	3.74	9.06	14.09	6.36
carbon dioxide	1,3,5-trimethylbenzene	24	1.54903	3.46	1.2531	11.01	4.29	7.27	14.10	10.57	13.33
carbon dioxide	trinervonin	38	1.18302	3.47	0.3962	2.77	2.86	16.62	27.91	6.58	163.95
carbon dioxide	triolein	10	1.08149	0.89	0.4442	-1.58	1.26	26.03	13.52	5.95	139.27
carbon dioxide	ubiquinone CoQ10	80	1.10732	2.57	0.6220	16.09	4.09	13.90	23.98	7.87	141.53
carbon dioxide	*n*-undecane	5	0.50642	4.69	4.1553	38.28	1.85	40.94	30.82	29.69	35.87

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ ($erg \cdot mol^{-1}$)	AARD	$B \times 10^{7}$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD
carbon dioxide	6-undecanone	13	0.43779	6.11	2.8101	31.76	2.53	36.53	25.70	28.03	27.81
carbon dioxide	vanillin	15	1.32242	2.67	1.5345	21.13	2.03	12.64	21.65	2.63	10.92
carbon dioxide	vitamin K_1	16	1.02045	1.56	0.8940	16.80	2.22	27.19	4.19	9.99	106.89
carbon dioxide	vitamin K_3	20	1.02163	1.82	1.1807	8.84	2.70	9.77	7.48	8.88	24.21
carbon dioxide	water	24	1.90681	8.69	8.3239	36.48	4.18	56.20	19.65	25.73	25.10
carbon dioxide	*m*-xylene	12	1.61990	5.75	0.7183	-34.12	10.53	17.73	23.95	14.94	52.18
water	acetamide	4	15.18960	9.31	50.0463	17.93	8.37	7.43	19.39	-	-
water	acetone	4	15.18570	6.63	19.9393	17.68	1.66	6.28	15.21	-	-
water	alanine	6	15.20150	0.83	21.7950	17.82	1.56	28.16	10.71	-	-
water	alloisoleucine	6	15.27030	1.11	18.2446	17.83	1.88	2.49	0.82	-	-
water	allothreonine	6	15.20180	0.81	19.3845	17.83	1.68	12.34	4.70	-	-
water	2-amino-2-methyl-1-propanol	5	15.41870	3.31	17.4820	17.77	1.30	6.91	1.39	-	-
water	α-amino-*n*-butyric acid	6	15.25050	0.84	20.1748	17.83	1.74	9.32	1.31	-	-
water	ammonia	5	15.75240	3.76	35.2132	17.78	2.43	36.59	2.95	-	-
water	arabinose	6	14.99710	3.25	18.7419	17.85	12.22	4.11	0.84	-	-
water	argon	8	15.12280	1.72	52.6166	17.92	6.47	50.62	9.05	-	-
water	benzene	24	14.92290	3.85	25.5613	17.82	9.46	11.04	19.97	-	-
water	benzoic acid	12	14.55570	2.85	26.4755	17.86	2.70	15.72	20.45	-	-
water	biphenyl	7	14.84000	3.94	18.6941	17.82	8.84	19.85	19.05	-	-
water	*n*-butane	16	15.74980	8.66	32.4055	17.91	9.89	11.19	8.86	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ $(\mathrm{erg \cdot mol^{-1}})$	AARD	$B \times 10^{7}$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^3 \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD
water	1,2-butanediol	5	15.18850	5.55	20.5739	17.82	11.67	2.19	6.80	-	-
water	1,3-butanediol	5	15.33520	2.04	19.1949	17.79	2.14	8.11	0.81	-	-
water	1,4-butanediol	5	15.24420	4.98	20.5989	17.82	10.83	2.28	6.84	-	-
water	1-butanol	13	15.39620	4.14	22.6052	17.83	9.31	3.81	7.93	-	-
water	*n*-butylbenzene	7	15.11350	4.34	18.6153	17.84	8.84	15.23	14.52	-	-
water	caffeine	22	14.67340	1.56	17.1205	17.80	2.35	10.24	9.78	-	-
water	camphor	8	14.77280	2.98	23.8525	17.87	3.84	14.43	14.88	-	-
water	carbon dioxide	111	14.22460	3.84	48.2267	17.84	5.36	3.74	25.65	-	-
water	cinnamic acid	8	14.37090	6.58	34.5188	17.91	3.15	27.64	28.41	-	-
water	α-cyclodextrin	4	14.61850	1.89	6.2131	17.74	5.85	9.31	16.97	-	-
water	β-cyclodextrin	4	14.57240	2.40	8.5327	17.84	2.64	17.31	7.20	-	-
water	cyclohexane	10	15.23230	6.45	25.5002	17.87	10.39	7.11	12.94	-	-
water	cyclopentane	10	15.30800	2.82	26.8344	17.87	7.95	4.38	11.66	-	-
water	diethylene glycol	5	15.05930	1.41	18.9049	17.78	0.80	2.86	4.68	-	-
water	*N*,*N*-diethylethanolamine	5	15.39270	2.83	15.3818	17.78	2.08	3.22	1.51	-	-
water	diglycolamine	5	15.33640	3.35	16.5597	17.76	0.68	7.44	1.87	-	-
water	2,2-dimethyl-1-propanol	6	15.28490	4.81	23.5633	17.86	13.18	5.26	11.22	-	-
water	dimethylethanolamine	5	15.59920	4.73	14.6623	17.74	3.18	18.36	9.25	-	-
water	dipropylene glycol	5	15.19380	2.90	13.7610	17.72	0.57	3.28	2.67	-	-
water	*meso*-erythritol	5	15.11860	5.11	17.9133	17.81	11.15	9.36	1.89	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^{7}$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
water	ethane	16	15.60170	4.69	34.7778	17.85	9.04	7.15	13.63	-	-
water	ethanol	22	15.36450	5.30	23.5426	17.75	4.57	10.84	7.98	-	-
water	ethylbenzene	16	15.13200	5.31	19.5821	17.82	10.85	9.52	13.20	-	-
water	ethylene glycol	9	15.26030	3.05	23.0235	17.78	1.81	13.69	3.10	-	-
water	1-ethylnaphthalene	7	15.03130	4.52	17.7474	17.83	9.10	16.37	15.01	-	-
water	formamide	4	14.69600	6.04	57.6636	17.91	9.03	17.85	31.85	-	-
water	fructose	4	15.06350	0.72	16.3981	17.83	0.40	23.17	17.23	-	-
water	galactose	6	15.02140	3.85	17.1534	17.85	12.76	1.18	0.98	-	-
water	glucose	10	15.08380	2.33	16.6379	17.84	8.22	10.02	7.44	-	-
water	glycerol	10	15.14470	3.89	21.2153	17.81	7.37	6.57	3.80	-	-
water	glycine	6	15.06200	1.13	24.1650	17.81	2.04	2.85	9.10	-	-
water	hexafluorobenzene	6	14.40790	4.03	18.7065	17.77	4.16	4.55	9.85	-	-
water	1,2,6-hexanetriol	5	15.23370	3.09	16.5032	17.80	2.32	1.66	2.90	-	-
water	homoserine	6	15.08770	0.76	19.8781	17.83	1.66	6.55	0.52	-	-
water	hydrogen	6	15.60540	2.25	137.2697	17.86	1.86	52.92	66.81	-	-
water	hydrogen sulfide	22	14.66060	9.08	28.1220	17.66	5.75	8.41	22.44	-	-
water	*myo*-inositol	5	15.02540	4.31	15.8241	17.83	10.32	8.28	5.65	-	-
water	isobutyramide	4	15.38290	13.45	43.2234	17.94	10.39	10.33	12.94	-	-
water	isoleucine	6	15.25940	0.97	18.4523	17.84	1.63	2.12	1.07	-	-
water	krypton	6	13.62610	3.98	62.5603	17.90	1.90	6.33	20.31	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_\mathrm{a} \times 10^{-10}$ $(\mathrm{erg \cdot mol^{-1}})$	AARD	$B \times 10^{7}$ $(\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}})$	V_D $(\mathrm{cm^{3} \cdot mol^{-1}})$	AARD	AARD	AARD	AARD	AARD
water	lactose	5	14.70880	1.07	12.4908	17.80	1.62	1.73	7.59	-	-
water	leucine	6	15.29590	1.14	18.2549	17.84	1.69	2.83	1.25	-	-
water	*tert*-leucine	6	15.28150	1.55	18.5315	17.84	2.18	4.10	1.68	-	-
water	mannitol	5	15.07300	4.76	15.1837	17.82	10.76	5.35	4.19	-	-
water	mannose	6	15.00720	3.73	17.2846	17.85	12.23	1.81	2.00	-	-
water	methane	32	15.81460	6.01	39.8491	17.82	5.73	7.89	18.76	-	-
water	methanol	15	15.17440	5.70	33.9363	17.79	6.69	6.02	17.61	-	-
water	methyl bromide	6	14.24850	6.68	59.8353	17.93	1.90	5.26	17.14	-	-
water	methyl chloride	6	14.97690	8.24	65.0273	17.94	1.49	10.40	12.84	-	-
water	methyl fluoride	6	14.87280	11.15	87.3643	17.95	2.14	8.93	23.78	-	-
water	2-methyl-1-butanol	6	15.21610	4.26	24.2610	17.87	12.05	6.51	12.39	-	-
water	2-methyl-2-butanol	6	15.34620	4.87	23.4421	17.87	12.76	4.13	8.13	-	-
water	3-methyl-1-butanol	6	15.30520	4.29	23.4173	17.86	12.61	4.72	10.72	-	-
water	2-methyl-2,4-pentanediol	5	15.36040	1.52	17.2307	17.81	1.94	1.98	1.44	-	-
water	3-methyl-2-butanol	6	15.26320	4.47	24.0493	17.87	12.62	5.32	11.28	-	-
water	2-methyl-2-propanol	9	15.55820	6.46	20.5461	17.82	11.38	7.12	5.17	-	-
water	methylcyclopentane	10	15.40330	3.24	23.6457	17.86	10.50	4.36	10.77	-	-
water	*N*-methylpyrrolidone	5	14.98960	2.31	19.9466	17.78	2.13	4.59	11.12	-	-
water	monoethanolamine	5	15.03210	6.66	17.9064	17.64	4.50	6.69	13.88	-	-
water	monoisopropanolamine	5	15.67560	2.63	18.5617	17.80	0.73	12.21	3.11	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ ($\mathrm{erg \cdot mol^{-1}}$)	AARD	$B \times 10^{7}$ ($\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$)	V_D ($\mathrm{cm^3 \cdot mol^{-1}}$)	AARD	AARD	AARD	AARD	AARD
water	naphthalene	7	14.76560	4.04	21.1846	17.82	8.83	20.42	22.32	-	-
water	2-naphthol	16	14.12700	2.63	24.4283	17.80	3.97	28.55	31.40	-	-
water	neon	6	13.35750	1.17	99.3936	17.84	1.81	21.76	48.89	-	-
water	nitrous oxide	78	14.32730	8.30	51.5695	17.86	7.19	8.77	24.98	-	-
water	norleucine	6	15.28670	0.93	18.1508	17.83	1.57	1.97	1.00	-	-
water	norvaline	6	15.28910	0.82	19.2053	17.83	1.56	5.74	1.15	-	-
water	oxygen	34	14.67270	6.60	36.2355	17.75	5.76	18.28	14.66	-	-
water	pentaerythritol	6	15.24940	5.14	16.4411	17.80	10.25	2.71	1.32	-	-
water	*n*-pentane	8	15.37920	8.93	29.6614	17.90	12.01	8.36	12.50	-	-
water	1-pentanol	6	15.21610	4.72	24.3166	17.86	12.44	6.94	12.84	-	-
water	2-pentanol	6	15.24050	4.65	23.2386	17.86	13.64	5.36	11.30	-	-
water	3-pentanol	6	15.27340	4.39	23.8842	17.87	12.73	4.97	10.78	-	-
water	piperazine	5	15.59230	5.15	14.6156	17.73	3.03	13.89	5.73	-	-
water	2-piperidineethanol	5	15.33090	1.95	15.7182	17.78	1.56	3.33	1.10	-	-
water	propanamide	4	15.24150	12.74	48.1588	17.94	10.44	10.72	16.68	-	-
water	propane	16	15.62870	6.78	34.5000	17.89	9.03	7.84	9.73	-	-
water	1-propanol	15	15.38850	4.79	23.5001	17.81	9.66	6.67	7.35	-	-
water	2-propanol	12	15.45520	5.46	24.8727	17.83	9.52	7.63	7.46	-	-
water	propylene glycol	5	15.24130	1.05	22.2593	17.80	0.64	9.24	3.10	-	-
water	radon	6	13.28640	7.40	52.0612	17.92	1.94	14.03	7.89	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ (erg·mol^{-1})	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3· mol^{-1})	AARD	AARD	AARD	AARD	AARD
water	salicylic acid	13	14.19100	2.53	27.1229	17.84	3.16	24.96	28.35	-	-
water	serine	6	15.10970	0.65	20.8117	17.82	1.53	13.69	2.92	-	-
water	sucrose	10	14.83750	3.36	13.1087	17.83	8.82	6.14	2.53	-	-
water	sulfolane	5	14.57730	2.16	19.9504	17.77	2.63	7.56	14.68	-	-
water	sulfur dioxide	4	13.90380	0.92	49.6045	17.86	0.50	10.51	29.43	-	-
water	tetraethylene glycol	5	15.21840	1.29	13.5617	17.79	0.64	2.31	5.47	-	-
water	threonine	6	15.19250	0.87	19.4005	17.83	1.78	15.44	6.82	-	-
water	toluene	15	15.15230	5.55	22.1708	17.84	12.32	6.36	12.78	-	-
water	triethanolamine	5	15.25480	2.40	14.6247	17.77	1.51	0.52	0.50	-	-
water	triethylene glycol	5	15.23650	2.57	13.5011	17.74	0.53	5.38	4.14	-	-
water	valine	6	15.28280	1.08	19.4018	17.84	1.80	6.27	1.29	-	-
water	xenon	6	13.64180	5.45	53.5845	17.91	1.88	13.72	10.79	-	-
water	xylitol	5	15.05460	4.66	16.5785	17.81	10.60	2.21	1.94	-	-
water	xylose	6	15.05860	4.03	18.4174	17.85	12.82	2.85	0.91	-	-
water	[Bmim][BF_4]	11	13.49060	1.78	25.0194	17.81	3.67	49.02	46.05	-	-
water	[Bmim][bti]	18	13.43440	4.77	19.6922	17.81	6.39	50.31	43.47	-	-
water	[Bmim][CF_3SO_3]	5	13.87720	4.02	11.7382	17.58	1.87	38.09	32.90	-	-
water	[Bmim][Cl]	6	13.74000	0.69	26.6577	17.82	3.66	47.14	45.43	-	-
water	[Bmim][MeSO4]	5	13.84630	5.34	11.3579	17.50	0.94	42.16	37.81	-	-
water	[Bmim][OcSO4]	6	13.81570	4.43	21.5140	17.84	5.18	51.51	43.66	-	-

Table 2 (*Continued*)

System			This Work (Eqs. (5) + (2) – (4))		DHB (Eq. (17))			WC (Eq. (6))	TC (Eq. (8))	HYS (Eqs. (15) and (16))	Zhu (Eq. (9) – (14))
Solvent (1)	Solute (2)	NDP	$E_a \times 10^{-10}$ ($erg \cdot mol^{-1}$)	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD
water	[Bmim][PF_6]	5	13.27840	1.12	23.0507	17.78	1.16	51.83	47.65	-	-
water	[Emim][BF_4]	5	13.47760	2.84	19.4488	17.66	1.10	46.75	45.51	-	-
water	[Emim][bti]	18	13.34060	4.50	21.2219	17.81	6.07	49.49	43.76	-	-
water	[Emim][$C_2H_5SO_4$]	11	13.75240	3.31	21.6441	17.80	4.08	42.67	39.25	-	-
water	[Emim][C_2N_3]	5	13.88400	0.95	22.0798	17.76	0.82	44.06	41.74	-	-
water	[Emim][CF_3SO_3]	5	13.50020	2.42	24.9967	17.83	2.00	43.45	40.45	-	-
water	[Emim][$MDEGSO_4$]	5	13.73430	2.30	19.2709	17.80	2.35	43.83	37.63	-	-
water	[Hmim][bti]	6	13.48890	1.40	17.8766	17.81	3.96	49.59	41.55	-	-
water	[Omim][bti]	6	13.52430	2.83	15.2296	17.77	4.55	49.86	40.85	-	-

For the 289 systems and 5485 data points used in the validation of our 1-parameter model, the grand AARD found is only 3.56% (see Table 3), which demonstrates its great accuracy since it is well inside the experimental error. Concerning the models adopted for comparison, the deviations achieved with the predictive models of Wilke-Chang, Tyn--Calus, He-Yu-Su, and Zhu *et al.* are 12.95%, 15.47%, 9.20% and 37.88%, respectively, while the 2-parameter correlation of Dymond offers 4.27%. The two hydrodynamic equations (WC and TC) provide similar results, and the He-Yu-Su correlation gives rise to the lowest deviations found in the family of predictive models. The small deviations obtained with Dymond's equation point out its correlation ability but should be also attributed to the fact it embodies two parameters.

Table 3. Calculated errors (AARD): global results per solvent and grand averages.

Solvent	NS	NDP	This Work (Eqs. (5) + (2) – (4))	DHB (Eq. (17))	WC (Eq. (6))	TC (Eq. (8))	HYS Eqs. (15) – (16))	Zhu (Eq. (9) – (14))
Supercritical CO_2	166	4323	3.39	3.80	12.84	15.03	9.20	37.88
Liquid H_2O	123	1162	4.18	6.00	13.36	17.08	–	–
Global	289	5485	3.56	4.27	12.95	15.47	9.20	37.88

NS = number of systems; NDP = number of data points; AARD = average absolute relative deviation.

In order to illustrate the good behavior of the new model, the calculated *versus* experimental diffusivities are plotted in Figures 1.a and 1.b for the two solvents considered. From these representations it is possible to observe in both cases the significant distribution of points along the diagonals, which emphasizes the unbiased behavior of the new model.

Taking into account the low AARDs obtained with the Dymond's equation (4.27%) and the new model (3.56%), a very stringent test has been accomplished to analyze their predictive ability. The following procedure was implemented: (1st) For 156 systems – for which there are points at various temperatures – the parameters E_a (new model) and B and V_D (DHB model) were fitted to the data at the highest temperature. This is the so-called partial fitting in Table 4. (2nd) These parameters were used to calculate the tracer diffusion coefficients of the 156 systems at all temperatures. (3rd) These deviations are

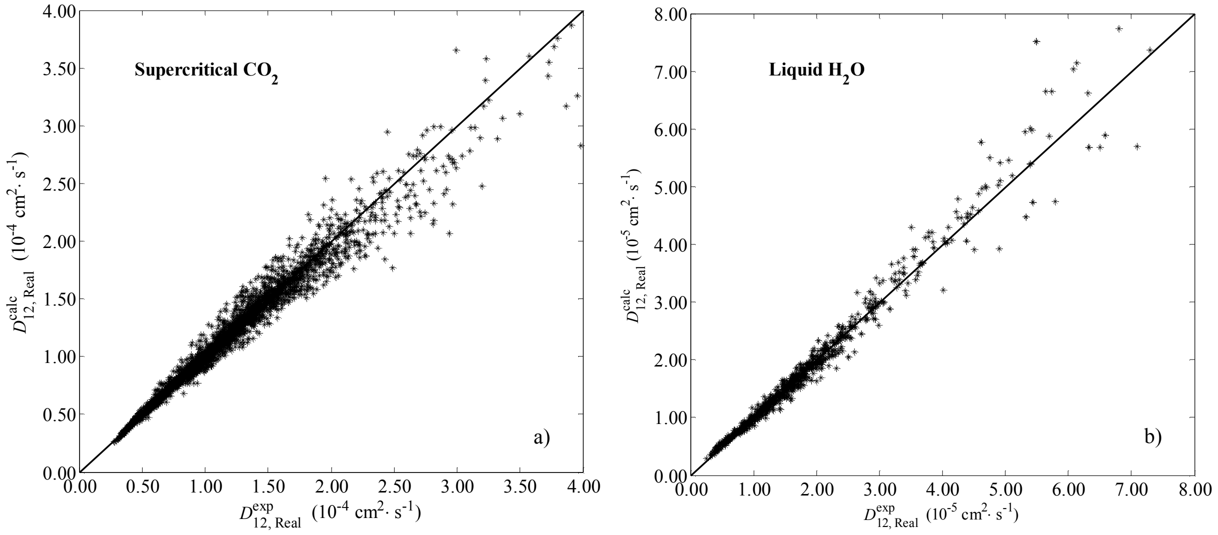

Figure 1. Calculated *versus* experimental tracer diffusivities for the new model developed in this work: Eqs. (5) + (2) – (4). Solvents: a) supercritical carbon dioxide (166 systems and 4323 data points) and b) liquid water (123 systems and 1162 data points).

Table 4. Global deviations achieved using parameters fitted to the following data base: *i*) all points of 156 systems for which there exist data at several temperatures; in this case, the parameters are those given in Table 2; *ii*) points for the highest temperature of 156 systems.

Model	AARD (%) (total fitting)	AARD (%) (partial fitting)
This work : Eqs. (5) + (2)-(4)	3.23	3.54
Dymond: Eq. (17)	4.41	10.40

compared in Table 4 with those obtained using the original total fitting approach, *i.e.* by averaging the AARDs already listed in Table 2. The final results evidence that the prediction capability of the Dymond's model is very fragile since its global AARD increases from 4.41% to 10.40%, while our new model rises from 3.23% to only 3.54%.

In the following, four distinct systems were specifically selected to illustrate graphically to behavior of the new model. In Figures 2.a and 2.b, the experimental diffusivities of $\alpha-$linolenic acid in SC-CO$_2$, and [Emim][bti] in liquid water, respectively, are plotted against solvent density. Notwithstanding in both cases the solutes particles are very asymmetrical and much bigger than the solvent molecules, the representations achieved by the model are very accurate. In Figures 2.c and 2.d, similar plots are given for 2-nitroanisole in SC-CO$_2$, and benzene in liquid water, respectively. With regard to the system CO$_2$/2-nitroanisole, the solute exhibits a large dipole moment while solvent is apolar [$\mu(C_7H_7NO_3) = 4.83$ Debye [73] and $\mu(CO_2) = 0.00$ Debye [44]], whereas in the second example the opposite occurs. In this case, the solvent is polar, $\mu(\mathrm{H_2O}) = 1.80$ Debye [44], and solute is nonpolar, $\mu(\mathrm{C_6H_6}) = 0.00$ Debye [44]. Once again, modeled results are in excellent agreement with experimental data.

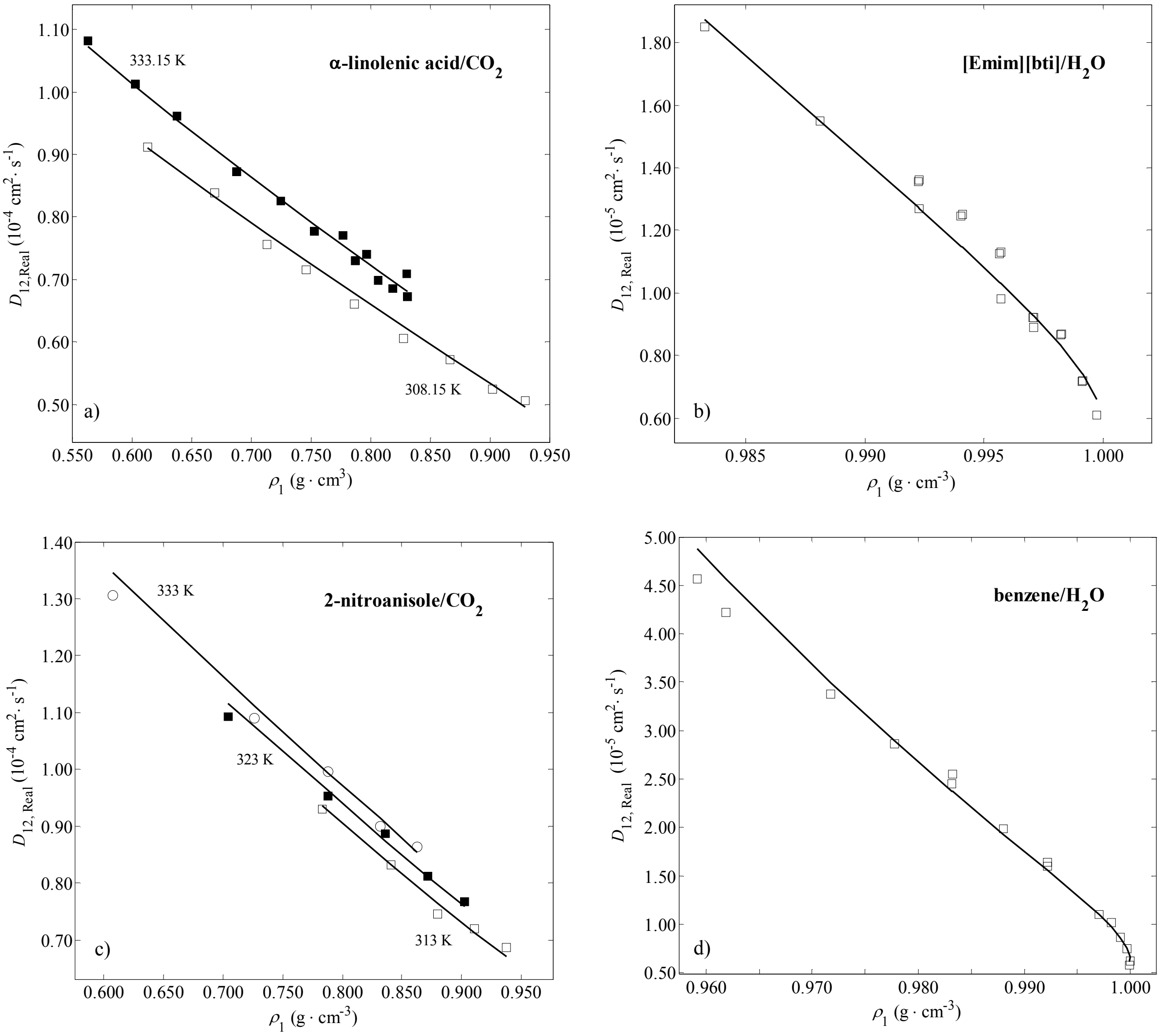

Figure 2. Tracer diffusivities against solvent density at constant temperatures or constant pressure for: a) α-linolenic acid in SC-CO$_2$; b) [Emim][bti] in liquid water; c) 2-nitroanisole in SC-CO$_2$; and d) benzene in liquid water. Points: experimental data; lines: new model, Eqs. (5) + (2) – (4).

4.PV.6. Conclusions

In this work a free-volume model for tracer diffusion coefficients in supercritical carbon dioxide and liquid water was proposed. It is explicit, very simple to use, and only requires temperature, solvent density, solute molecular weight, and solvent LJ force constants. The unique parameter per system is the activation energy. The validation of the model was carried out with 289 binary systems and 5485 experimental diffusivities, and evidenced its high accuracy. The grand AARD is only 3.56% for the whole database, where very asymmetrical and distinct polarity systems are included. The global results achieved by other equations adopted for comparison are much higher except for Dymond's correlation: AARD (Wilke-Chang) = 12.95%, AARD (Tyn-Calus) = 15.47%, AARD (He-Yu-Su) = 9.20%, AARD (Zhu *et al.*) = 37.88%, AARD (Dymond) = 4.27%. Nonetheless, it was shown that Dymond's model should not be used for prediction calculations, since its average deviation jumps to 10.40%. In contrast, our equation only rises to 3.54%, which confirms its fine predictive capability.

Nomenclature

A, γV_1^*	Solvent specific parameters of Eq. (5) (Table 1), $\mathrm{cm^2 \cdot g^{0.5} \cdot s^{-1} \cdot mol^{-0.5} \cdot K^{-0.5}}$ and $\mathrm{cm^3 \cdot mol^{-1}}$, respectively
A'	Parameter in Eq. (15)
AARD	Average absolute relative deviation, $\mathrm{AARD} = (100/\mathrm{NDP}) \times \sum_{i=1}^{\mathrm{NDP}} \left\| D_{12,\,\mathrm{Real}}^{\mathrm{cal}} - D_{12,\,\mathrm{Real}}^{\mathrm{exp}} / D_{12,\,\mathrm{Real}}^{\mathrm{exp}} \right\|_i$, %
B	Parameter in Eq. (17), $\mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$
B'	Parameter in Eq. (16)
D_{12}	Tracer diffusion coefficient, $\mathrm{cm^2 \cdot s^{-1}}$
E_a	Activation energy, $\mathrm{erg \cdot mol^{-1}}$
k	Exponent/parameter in Eq. (15)
k_B	Boltzmann constant, $1.380658 \times 10^{-16}\ \mathrm{erg \cdot K^{-1}}$
LJ	Lennard-Jones
M	Molecular weight, $\mathrm{g \cdot mol^{-1}}$
m_1	Mass of solvent molecule, g
N_a	Avogadro constant, $6.0221367\ \times 10^{23}\ \mathrm{mol^{-1}}$
NDP	Number of data points
NS	Number of systems
p_j	Probability given by Eq. (1)
P	Pressure, bar
P	Parachor
$\Re_\mathrm{g}$	Universal gas constant, $8.31541 \times 10^7\ \mathrm{erg \cdot mol^{-1} \cdot K^{-1}}$
T	Temperature, K
u	Particle velocity, $\mathrm{cm \cdot s^{-1}}$
v^*	Molecular critical free volume, $\mathrm{cm^3}$
V	Molar volume, $\mathrm{cm^3 \cdot mol^{-1}}$
V_D	Parameter in Eq. (19), $\mathrm{cm^3 \cdot mol^{-1}}$

Greek Letters

ε^*	Molecular critical energy, erg
$\varepsilon / k_\mathrm{B}$	Lennard-Jones energy parameter, K

φ	Hard-sphere packing fraction
ϕ_1	Association factor of the solvent
γ	Correction factor for the free volume
η	Viscosity, cP
σ	Lennard-Jones diameter, cm
ρ	Number density, cm^{-3}

Subscripts

1	Solvent
2	Solute
12	Binary property
bp	Boiling point
c	Critical property
eff	Refers to the effective hard sphere diameter
LJ	Lennard-Jones
r	Reduced property (using critical constants)
Real	Refers to real systems

Superscripts

$*$	Reduced property (using LJ parameters)

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Paper VI

Adapted from

Universal Model for Accurate Calculation of Tracer Diffusion Coefficients in Gas, Liquid and Supercritical Systems

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Abstract

In this work it is presented a new model for accurate calculation of binary diffusivities (D_{12}) of solutes infinitely diluted in gas, liquid and supercritical solvents. It is based on a Lennard-Jones (LJ) model, and contains two parameters: the molecular diameter of the solvent and a diffusion activation energy. The model is universal since it is applicable to polar, weakly polar, and non-polar solutes and/or solvents, over wide ranges of temperature and density. Its validation was accomplished with the largest database ever compiled, namely 487 systems with 8293 points totally, covering polar (180 sytems/2335 points) and non-polar or weakly polar (307 systems/5958 points) mixtures, for which the average errors were 2.65% and 2.97%, respectively. Furthermore, the model exhibited excellent prediction ability. Ten expressions from the literature were adopted for comparison, but provided worse results or were not applicable to polar systems. A spreadsheet for D_{12} calculation is provided online for users in the Supplementary Material.

4.PVI.1. Introduction

Transport coefficients are fundamental properties for simulation, design and scale-up of rate-controlled separations and multiphase reaction processes. In particular the infinitely dilute (tracer) diffusion coefficient of a solute in a solvent is one of the most important transport properties. While in numerous industrial applications the systems are very dilute, which happens for instance in supercritical fluid extraction, for most concentrated liquid mixtures the diffusion coefficients can be estimated based on their individual tracer diffusivities using, for example, the Darken [1] or the Vignes [2] mixing rules. Accordingly, a number of equations have been proposed to describe tracer diffusion coefficients due to their chief relevance.

At low densities, the diffusion coefficients for gaseous systems can be reasonably estimated by the kinetic theory of Enskog or by a number of modifications available in the literature [3-5]. On the other hand, for dense fluids no satisfactory theory is known even for the simple hard sphere fluid, given the many-body interactions involved and the lack of pair potential energy functions for complex molecules. As a result, the expressions adopted for these systems are frequently empirical or semi-empirical [3, 5-6], while theoretically sound equations are most desirable in order to possess interpolation and predictive ability.

The main approaches for dense fluids are the modified Enskog theory [5, 7-8], the effective hard sphere diameter method [5, 9], the free-volume approaches (*e.g.*, Dymond, Cohen–Turnbull, Macedo–Litovitz, Chung) [5, 10-14], the van der Waals [5, 8, 15] and rough hard sphere theories [5, 16], the hydrodynamic expressions based on the Stokes-Einstein equation [6, 17], the Eyring activated-state theory [18-19], models based on idealized fluids (*e.g.*, Hard Sphere, Square Well, Lennard-Jones, Repulsive Lennard-Jones or Weeks-Chandler-Andersen) [3, 5, 20-27], and the excess entropy scaling laws which are receiving much attention recently [28-32].

The equations found in the literature are usually applicable over restricted ranges of temperature and density, being in many cases specific for a particular physical state or inadequate to represent polar systems [3, 5-6]. In recent years we have been publishing equations very adequate for gases and dense phases (liquid and supercritical fluids). In 1997 [21] and 2010 [25], the Liu-Silva-Macedo equation was developed and revisited, being applicable to liquid, gases, and supercritical fluids, and gave 3.89% of error. Then, in 2011, two models were published where one follows the approach of Rice and Gray, and the other one contains an attractive exponential term, being both valid for non-polar and weakly polar solvents [23-24]. Lately, Magalhães *et al.* [22] presented a new equation that can be used for systems where at least one of the two component is polar. The average deviation for 3463 data points was 3.65%.

In this work a universal model for tracer diffusion coefficients of polar and non-polar real systems is proposed. It is appropriate for gas, liquid, and supercritical phases, and very accurate over wide ranges of temperature and density. The largest database ever published was compiled for the validation of the proposed model (487 systems with 8293 experimental points). A spreadsheet for D_{12} calculation was prepared and is provided online for users in Supplementary Material.

4.PVI.2. New Model for Tracer Diffusion Coefficients of Real Polar and Non-polar Systems

In this section the new model for the calculation of tracer diffusion coefficients of real systems is developed. It is intended to be applicable to mixtures composed of polar and/or non-polar molecules, which can also be extremely distinct in terms of size and symmetry. Firstly, an expression for the Lennard-Jones system is proposed, and then it is extended to real binary systems.

4.PVI.2.1. Tracer diffusivity model for LJ system, $D_{12,\mathrm{LJ}}$

The Hard-Sphere (HS) tracer diffusivity of a solute (2) through a solvent (1), $D_{12,\mathrm{HS}}$, is usually obtained from Enskog theory, $D_{12,\mathrm{E}}$, combined with a correction factor, F_{12}, dependent upon the reduced density of the solvent, ρ_1^*, and on size and mass ratios:

$$D_{12,\mathrm{HS}} = D_{12,\mathrm{E}} \times F_{12}\left(\rho_1^*, \sigma_2/\sigma_1, m_2/m_1\right) \tag{1}$$

where σ_i and m_i are the diameter and mass of molecule i, respectively, $\rho_1^* = \rho_1 \sigma_1^3$ is the reduced number density of the solvent, and ρ_1 is the solvent number density.

According to Kushick and Berne [33] and Straub [34], the attractive forces play an important role in the transport process, especially at low temperatures. Several functions have been proposed in literature to take them into account in order to derive models for the LJ fluid (*e.g.* Straub [34], Speedy *et al.* [35], Liu *et al.* [27], Silva and Liu [5]). In this work an exponential factor was selected to embody this attractive contribution: $\exp\left(-\alpha_{12}/T_{12}^*\right)$, where α_{12} is one parameter and T_{12}^* is a reduced temperature to be defined in the following. Furthermore, the characteristic softness of the LJ molecules was also taken into account by introducing effective hard sphere diameters, $\sigma_{i,\mathrm{eff}}\left(i = 1, 2\right)$, in the HS model, which depend on the temperature and eventually on the density. Hence, the final model for the tracer diffusivity of the LJ systems is:

$$D_{12,\mathrm{LJ}} = D_{12,\mathrm{E}} \times F_{12}\left(\rho_{1,\mathrm{eff}}^*, \sigma_{2,\mathrm{eff}}/\sigma_{1,\mathrm{eff}}, m_2/m_1\right) \times \exp\left(-\frac{\alpha_{12}}{T_{12}^*}\right) \tag{2}$$

In the following, the subsidiary equations necessary for the calculations are presented. All of them are written in terms of HS effective diameters since they are used to represent the LJ system.

i) Enskog equation for $D_{12,\mathrm{E}}$. Enskog [5, 7-8] corrected the ideal gas behaviour by taking into account excluded molecular volume effects, which are increasingly important as density raises, and by modifying the collision frequency in the fluid by the unlike pair radial distribution function at contact, $g(\sigma)$. In terms of effective diameters, the Enskog diffusivity is:

$$\frac{\rho_1 D_{12,\mathrm{E}}}{\rho_1^0 D_{12}^0} = \frac{1}{g(\sigma_{12,\mathrm{eff}})} \tag{3}$$

where superscript "0" denotes ideal gas, and $\sigma_{12,\mathrm{eff}}$ is the binary effective HS diameter. The binary diffusivity of ideal gases, D_{12}^0, can be calculated by the rigorous kinetic theory of gases [4-5]. Once again, in terms of effective diameter it is:

$$\rho_1^0 D_{12}^0 = \frac{3}{8\sigma_{12,\mathrm{eff}}^2}\left(\frac{k_\mathrm{B} T}{2\pi m_{12}}\right)^{1/2} \quad , \; m_{12} = \frac{m_1 m_2}{m_1 + m_2} = \frac{1}{N_\mathrm{a}}\frac{M_1 M_2}{M_1 + M_2} \tag{4}$$

being k_B the Boltzmann constant, T the absolute temperature, and m_{12} the reduced mass of the system, M_i the molecular weight of component i, and N_a the Avogadro constant.

ii) Radial distribution function at contact. In this paper, $g(\sigma_{12,\mathrm{eff}})$ is calculated by the expression of Mansoori *et al.* [36], due to its simplicity and accuracy. It depends on the effective HS packing fraction of the solvent, $\varphi_{1,\mathrm{eff}}$, and effective diameters ratio:

$$g(\sigma_{12,\mathrm{eff}}) = \frac{1}{(1-\varphi_{1,\mathrm{eff}})^3}\left(1-\varphi_{1,\mathrm{eff}} + \frac{2\varphi_{1,\mathrm{eff}}}{1+\sigma_{1,\mathrm{eff}}/\sigma_{2,\mathrm{eff}}}\right)\left(1-\varphi_{1,\mathrm{eff}} + \frac{\varphi_{1,\mathrm{eff}}}{1+\sigma_{1,\mathrm{eff}}/\sigma_{2,\mathrm{eff}}}\right) \tag{5}$$

For N_1 spheres occupying a volume V , $\varphi_{1,\mathrm{eff}}$ is given by:

$$\varphi_{1,\mathrm{eff}} = \frac{N_1 \pi \sigma_{1,\mathrm{eff}}^3}{6V} = \frac{\pi}{6}\rho_1 \sigma_{1,\mathrm{eff}}^3 = \frac{\pi}{6}\rho_{1,\mathrm{eff}}^* \tag{6}$$

iii) F_{12} correction factor. Several equations are available in the literature for F_{12} [5, 24, 37-40]. The F_{12} correlation of Magalhães *et al.* [24] has been adopted, since it is simple, explicit and very accurate in comparison to several well known models from literature as those by Sung and Steel [40], Sun and Chen [39], Easteal and Woolf [37], and Eaton and Akgerman [38]. Once again, in terms of $\sigma_{i,\mathrm{eff}}$:

$$F_{12} = \frac{F_{11} + {\rho_{1,\mathrm{eff}}^*}^{1.7}\left[a \ln\left(\sigma_{2,\mathrm{eff}}/\sigma_{1,\mathrm{eff}}\right) + b \ln^2\left(\sigma_{2,\mathrm{eff}}/\sigma_{1,\mathrm{eff}}\right) + c \ln\left(m_2/m_1\right)\right]}{1 + {\rho_{1,\mathrm{eff}}^*}^{3.0}\left[d \ln\left(\sigma_{2,\mathrm{eff}}/\sigma_{1,\mathrm{eff}}\right)\right]^2} \tag{7}$$

where coefficients *a*, *b*, *c* and *d* are linear functions of the reduced number density of the solvent:

$$\begin{cases} a = -1.676382\rho_{1,\mathrm{eff}}^* + 1.638561 \\ b = -8.516830\rho_{1,\mathrm{eff}}^* + 8.631536 \\ c = -1.320347\rho_{1,\mathrm{eff}}^* + 1.351067 \\ d = -5.062546\rho_{1,\mathrm{eff}}^* + 5.409662 \end{cases} \tag{8}$$

and F_{11} is given by:

$$F_{11} = 1 + 0.94605{\rho_{1,\mathrm{eff}}^*}^{1.5} + 1.4022{\rho_{1,\mathrm{eff}}^*}^{3} - 5.6898{\rho_{1,\mathrm{eff}}^*}^{5} + 2.6626{\rho_{1,\mathrm{eff}}^*}^{7} \tag{9}$$

iv) Combining rules for the LJ parameters. The binary LJ diameter and energy are evaluated by the classical Lorentz-Berthelot combining rules:

$$\sigma_{12,\mathrm{LJ}} = \frac{\sigma_{1,\mathrm{LJ}} + \sigma_{2,\mathrm{LJ}}}{2} \tag{10}$$

$$\frac{\varepsilon_{12,\mathrm{LJ}}}{k_\mathrm{B}} = \sqrt{\left(\varepsilon_{1,\mathrm{LJ}}/k_\mathrm{B}\right) \times \left(\varepsilon_{2,\mathrm{LJ}}/k_\mathrm{B}\right)} \tag{11}$$

v) Effective HS diameter. As has been mentioned above, the softness of the repulsive interactions was considered using effective hard sphere diameters, derived from perturbation approaches. These usually combine HS models as an appealing and tractable first approximation, for the major excluded-volume and packing effects, with an effective diameter dependent on temperature and possibly on density, to account for the softness of the repulsive potential. Following Liu *et al.* [21, 27] and the extensive comparison carried out by Silva *et al.* [9], the temperature-dependent expression selected in this work is:

$$\sigma_{i,\mathrm{eff}}\left(T_i^*\right)=\sigma_{i,\mathrm{LJ}}\times 2^{\frac{1}{6}}\left[1+\left(1.3229\,T_i^*\right)^{\frac{1}{2}}\right]^{-\frac{1}{6}},\; i=1,2,12 \tag{12}$$

The expression is the same for solvent ($i=1$), solute ($i=2$), and binary system ($i=12$).

vi) Reduced number density and reduced temperature. The effective reduced number density of the solvent and the reduced temperatures embodied in the previous equations are defined by:

$$\rho_{1,\mathrm{eff}}^*=\rho_1\,\sigma_{1,\mathrm{eff}}^* \quad \text{and} \quad T_i^*=k_\mathrm{B}T/\varepsilon_{i,\mathrm{LJ}} \qquad i=1,2,12 \tag{13}$$

vii) LJ energy and diameter. The LJ energies for both solvent and solute ($i=1,2$) are estimated from their critical temperature [5, 20]; the LJ diameter of the solute ($i=2$) are estimated as function of the critical temperature and pressure [5, 20], or critical volume [6, 41-42]:

$$\frac{\varepsilon_{i,\mathrm{LJ}}}{k_\mathrm{B}}=0.774\,T_{\mathrm{c},i}\;, \quad i=1,2 \tag{14}$$

$$\sigma_{2,\mathrm{LJ}}^3(\text{Å}^3)=0.17791+11.779\left(\frac{T_\mathrm{c}}{P_\mathrm{c}}\right)-0.049029\left(\frac{T_\mathrm{c}}{P_\mathrm{c}}\right)^2 \quad \text{if} \quad T_{\mathrm{c},2}/P_{\mathrm{c},2}\le 100 \tag{15}$$

$$\sigma_{2,\mathrm{LJ}}(\text{Å})=0.809\,V_{\mathrm{c},2}^{1/3} \qquad \text{if} \quad T_{\mathrm{c},2}/P_{\mathrm{c},2}>100 \tag{16}$$

$T_{\mathrm{c},i}$, $P_{\mathrm{c},i}$, and $V_{\mathrm{c},i}$ are expressed in K, bar, and $\mathrm{cm^3\cdot mol^{-1}}$, respectively. On the other hand, the LJ diameter of the solvent, $\sigma_{1,\mathrm{LJ}}$, is taken as an adjustable parameter of the model.

4.PVI.2.2. New tracer diffusivity model for real systems, $D_{12,\mathrm{Real}}$

The final model for the tracer diffusion coefficient of real systems, $D_{12,\mathrm{Real}}$, can be now obtained from $D_{12,\mathrm{LJ}}$ by expressing directly the temperature and density on the core Eq. (2) (plus Eqs. (5), (7) – (9) and (12)) which is equivalent to substitute Eqs. (6) and (13). It is worth noting that the new model involves two parameters that may be fitted to experimental data: *i)* As mentioned above, $\sigma_{1,\mathrm{LJ}}$ is one parameter; *ii)* the second parameter, E_D, arises by manipulating the exponential term of Eq. (2) using Eq. (13). It can be taken as an activation energy of the diffusion process.

$$\exp\left(-\frac{\alpha_{12}}{T_{12}^{*}}\right)=\exp\left(-\frac{\alpha_{12}\,\varepsilon_{12,\mathrm{LJ}}/k_\mathrm{B}}{T}\right)=\exp\left(-\frac{E_\mathrm{D}}{\Re_\mathrm{g}\,T}\right) \qquad (17)$$

with $\Re_\mathrm{g}=N_\mathrm{a}\,k_\mathrm{B}$ being the universal gas constant. Therefore, the master equation of our 2-parameter model is:

$$D_{12,\mathrm{Real}}=\frac{3}{8\rho_1\sigma_{12,\mathrm{eff}}^{2}}\left(\frac{k_\mathrm{B}T}{2\pi m_{12}}\right)^{1/2}\times\frac{F_{12}}{g(\sigma_{12,\mathrm{eff}})}\times\exp\left(-\frac{E_\mathrm{D}}{\Re_\mathrm{g}\,T}\right) \qquad (18)$$

which may be expressed in condensed form as:

$$D_{12,\mathrm{Real}}=D_{12,\mathrm{Real}}\left[T,\rho_1;\sigma_{1,\mathrm{LJ}},E_\mathrm{D};m_1,m_2,T_{\mathrm{c},1},T_{\mathrm{c},2},P_{\mathrm{c},2},\mathrm{eventually}\,V_{\mathrm{c},2}\right] \qquad (19)$$

T and ρ_1 are the operating conditions, $\sigma_{1,\mathrm{LJ}}$ and E_D are the parameters, and the remaining variables are needed for the estimation of LJ diameters and energies, the correction term F_{12}, and the reduced mass of the system.

It is important to refer that readers may find in Supplementary Material a spreadsheet for the calculation of $D_{12,\mathrm{Real}}$ for the 487 systems studied in this work. The unique input data are: the number of the system according to Table S.1, the temperature, and the number density of the solvent.

4.PVI.2.3. Flux diagram of the new model for the calculation of $D_{12,\text{Real}}$

The calculation procedure of tracer diffusivities by our new model is summarized in the following flux diagram:

i) Define the system (1 = solvent, 2 = solute), and specify the temperature and number density of the solvent density (T, ρ_1).

ii) Collect the values of the mass of both molecules and their critical properties (m_1, m_2, $T_{c,1}$, $T_{c,2}$, $P_{c,1}$, $P_{c,2}$, and $V_{c,2}$). They are listed in Table S.2 (Supplementary Material).

iii) Take the two model parameters from Table 1: LJ diameter of the solvent, $\sigma_{1,\text{LJ}}$, and activation energy, E_D.

iv) Estimate the remaining LJ parameters ($\varepsilon_{1,\text{LJ}}/k_\text{B}$, $\varepsilon_{2,\text{LJ}}/k_\text{B}$, and $\sigma_{2,\text{LJ}}$) using Eqs. (14), and (15) or (16).

v) Compute the binary LJ parameters and the reduced mass of the system ($\sigma_{12,\text{LJ}}$, $\varepsilon_{12,\text{LJ}}/k_\text{B}$, m_{12}) by Eqs. (10), (11), and (4), respectively.

vi) Compute the reduced temperatures T_1^*, T_2^*, and T_{12}^* by Eq. (13).

vii) Compute the effective hard sphere diameters $\sigma_{1,\text{eff}}$, $\sigma_{2,\text{eff}}$, and $\sigma_{12,\text{eff}}$ by Eq. (12).

viii) Calculate the effective reduced number density of solvent, $\rho_{1,\text{eff}}^*$, by Eq. (13), and the effective hard sphere packing fraction of the solvent, $\varphi_{1,\text{eff}}$, by Eq. (6).

ix) Compute correction factor F_{12} by Eqs. (7) – (9).

x) Calculate the radial distribution function at contact, $g(\sigma_{12,\text{eff}})$, by Eq. (5).

xi) Calculate the tracer diffusivity of the systems, $D_{12,\text{Real}}$, by Eq. (18).

4.PVI.3. Model Validation: Database and Data for the Calculations

The new $D_{12,\text{Real}}$ model proposed in this work was validated using the largest database of tracer diffusivities published up till now, which comprehends 487 systems embodying a total of 8293 points, covering polar (180 sytems/2335 points) and non-polar or weakly polar (307 systems/5958 points) mixtures. Table S.2 (Supplementary Material) compiles the systems studied, number of data points (NDP), number of systems (NS), reduced ranges of temperature, pressure, and solvent density for each system (reduction performed with critical constants), and the data sources. In general all published data were used, excluding the systems with data available only in graphical form. Table S.2 (Supplementary Material) lists the name, molecular formula, CAS number, molecular weight, critical constants (T_c, P_c and V_c), molar volume at normal boiling point (V_bp) for all molecules involved in calculations (300 totally).

In the case the solvent densities had been not reported by the authors of the data used, they were calculated by the correlations of Pitzer and Schreiber [43] for CO_2, and Hankinson-Brobst-Thomson [6, 44] for other fluids. Concerning the non-reported viscosities, which are necessary for the hydrodynamic equations adopted for comparison in this work, they were estimated by the correlations of Mehrotra [45] for liquid hydrocarbons, and Altunin and Sakhabetdinov [46] for carbon dioxide. In addition, NIST and DIPPR databases were also used to estimate omitted density and viscosity data. The unknown molar volumes at normal boiling point were estimated by Tyn Calus equation [6, 47]. The unknown critical constants were estimated by Joback [6, 48-49], Somayajulu [50], Klincewicz [6, 51], Ambrose [6, 52-53], Wen-Qiang [54], and Constantinou-Gani [55] methods. For ionic liquids, the critical constants were taken from Valderrama and Rojas [56].

4.PVI.4. Results and Discussion

In this section, the results obtained with our universal model are presented and analysed. Additionally, ten tracer diffusivity expressions were adopted for comparison, namely: six predictive hydrodynamic equations: Wilke-Chang (WC) [6, 17, 57], Lusis-Ratcliff (LR) [17, 58], Lai-Tan (LT) [59], Tyn-Calus (TC) [6, 60], Scheibel (Sheib) [17, 61], and Reddy-Doraiswamy (RD) [17, 62]; the predictive equations of Zhu *et al.* (Zhu) [63] and He-Yu-Su (HYS) [64]; and the 2-parameter correlation of Dymond (Dym) [5, 8, 10, 17] and the 1-parameter $\mathrm{TLSM_d}$ model [5, 21, 25]. The expressions chosen for comparison are briefly described in Supplementary Material.

All detailed results are compiled in Table 1, namely, the deviations and the fitted parameters of the systems. The errors were quantified by the average absolute relative deviation, AARD:

$$\mathrm{AARD} = \frac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left| \left(D_{12,\,\mathrm{Real}}^{\mathrm{calc}} - D_{12,\,\mathrm{Real}}^{\mathrm{exp}} \right) \middle/ D_{12,\,\mathrm{Real}}^{\mathrm{exp}} \right|_i \tag{20}$$

The global results are listed in Tables 2 and 3, divided into systems involving non-polar or weakly polar solvents and systems containing polar solvents (Table 2), and into liquid, gaseous and supercritical systems (Table 3). The grand averages are also reported. In the following, these results are discussed in combination with graphical representations. Taking into account the global deviations shown in Table 2, one may conclude that our model achieved excellent results for all type of systems, whether polar or not: AARD (non-polar/weakly polar) = 2.65% for 307 systems and 5958 data points, and AARD (polar) = 2.97% for 180 systems and 2335 data points. The grand average is only 2.74% for the 487 systems and 8283 experimental diffusivity values. It is worth noting this important progress, since good equations for non-polar systems generally fail when extended to polar fluids [5, 21, 25, 59, 63]. Furthermore, excellent results were also found for all physical states of the systems (see Table 3): AARD (gas) = 1.56% for 73 systems and 1036 data points, AARD (supercritical) = 2.90% for 173 systems and 4398 data points, and AARD (liquid) = 2.92% for 241 systems and 2859 data points. Besides, small deviations were found for systems containing pairs of molecules with very different molecular weights. For instance, when solutes are ten times heavier than the solvent, the average absolute relative deviation found was merely 1.59% (NS = 53 and NDP = 762).

Table 1. Detailed results (Note: An hyphen means that model is not applicable.).

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
							Non-polar and weakly polar solvents											
acetylene	helium	7	3.64674	99.676	0.07	0.02672	0.11	16.6409	3988.91	0.12	64.15	–	–	–	–	–	–	–
argon	*i*-butane	8	3.91856	515.524	1.84	-0.08144	1.52	2.6722	5654.17	1.33	71.90	–	–	–	–	–	–	–
argon	*n*-butane	8	3.91856	406.577	1.37	-0.06433	1.39	2.8191	6520.36	1.24	67.17	–	–	–	–	–	–	–
argon	ethane	9	3.42069	491.433	1.13	-0.02437	1.35	4.7507	7729.39	1.72	12.61	–	–	–	–	–	–	–
argon	helium	49	3.04831	93.409	0.75	0.04758	0.94	20.3368	3529.83	1.43	69.37	–	–	–	–	–	–	–
argon	hydrogen	5	2.72595	192.786	1.35	0.01681	4.44	23.0413	3938.78	2.29	72.01	–	–	–	–	–	–	–
argon	krypton	11	3.64362	597.798	0.13	-0.04308	0.19	4.4393	6004.27	0.60	27.49	–	–	–	–	–	–	–
argon	methane	9	3.06670	635.774	1.56	0.00365	2.97	7.7281	8889.20	1.49	22.49	–	–	–	–	–	–	–
argon	neon	25	3.28773	264.257	1.05	-0.00474	2.00	10.3605	6724.28	5.46	35.22	–	–	–	–	–	–	–
argon	propane	9	3.42433	625.082	0.89	-0.01660	1.09	3.6775	7706.29	0.78	38.79	–	–	–	–	–	–	–
1,3-butadiene	helium	7	5.11702	70.447	0.04	-0.04447	0.06	10.5291	3742.45	0.08	74.31	–	–	–	–	–	–	–
n-butane	helium	7	5.64834	-131.305	0.09	-0.04914	0.81	9.2373	1884.23	0.19	99.08	–	–	–	–	–	–	–
carbon dioxide	acetone	178	3.41549	513.367	3.77	0.03450	4.15	2.1316	13.74	5.05	11.71	4.15	10.29	5.64	5.48	20.26	38.16	12.59
carbon dioxide	acridine	6	2.81791	1768.360	1.51	0.07836	1.95	1.2634	16.55	2.85	15.47	3.50	27.22	4.93	12.06	10.72	72.93	20.98
carbon dioxide	adamantanone	8	3.00942	175.872	2.26	0.25940	2.54	1.4379	-2.78	2.59	29.47	31.54	14.95	18.17	13.45	9.10	28.25	7.13
carbon dioxide	allylbenzene	15	2.86648	1580.768	1.98	0.06975	2.99	1.3060	10.81	3.34	10.60	4.39	16.32	5.36	8.42	11.96	62.71	17.71
carbon dioxide	aniline	15	2.85993	2177.966	2.24	-0.03356	2.98	1.1791	8.61	2.46	21.45	25.07	33.65	33.34	33.91	51.80	92.40	48.89
carbon dioxide	anisole	15	3.19828	1147.475	1.93	0.04685	2.06	1.4822	13.90	2.97	7.70	3.35	16.31	7.33	11.77	20.82	64.09	22.66
carbon dioxide	anthracene	22	3.44081	177.616	0.66	0.14875	3.88	1.6433	22.35	1.75	20.69	10.72	14.67	10.38	2.86	1.72	57.43	9.98

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	arachidonic acid (AA)	75	2.84263	1495.938	1.26	0.11673	2.13	0.8591	13.44	2.51	49.72	7.61	41.11	9.70	16.13	7.12	92.80	25.84
carbon dioxide	AA ethyl ester	48	3.24677	692.698	0.56	0.13294	2.43	1.1233	23.26	1.17	37.41	1.53	30.43	15.16	10.26	0.94	84.76	19.76
carbon dioxide	behenic acid ethyl ester	17	3.36660	309.722	0.72	0.14261	3.66	1.2263	27.32	0.86	65.88	2.73	31.30	21.34	5.03	6.43	78.86	14.66
carbon dioxide	benzene	222	2.99480	916.855	6.76	0.08974	7.45	1.4921	-1.03	7.59	11.77	10.21	9.70	9.14	9.23	13.21	40.08	11.09
carbon dioxide	benzoic acid	29	3.31644	776.459	5.74	0.09276	5.70	1.8170	21.69	6.34	8.54	6.05	14.24	9.27	13.02	21.26	65.32	23.35
carbon dioxide	benzyl acetate	15	3.22815	1098.622	2.00	0.05359	2.21	1.3600	16.99	3.02	9.82	3.24	28.09	7.79	17.75	20.20	78.14	27.69
carbon dioxide	benzylacetone	15	3.10086	1394.613	2.08	0.04500	2.32	1.0795	9.68	3.76	12.63	9.19	30.46	6.19	17.90	18.07	80.40	27.48
carbon dioxide	biphenyl	24	3.00008	1249.836	2.72	0.10845	3.41	1.3557	13.85	3.39	15.21	8.45	10.04	10.13	6.94	6.96	56.82	10.78
carbon dioxide	2-bromoanisole	15	3.14451	1341.592	2.13	0.05829	2.37	1.2561	12.79	3.66	10.23	11.27	30.69	16.52	23.81	30.64	83.97	35.12
carbon dioxide	bromobenzene	15	2.85085	1655.914	3.92	0.06305	4.63	1.4373	12.25	4.36	9.08	14.21	13.52	7.81	10.55	20.44	61.51	21.50
carbon dioxide	2-butanone	38	3.35084	456.078	1.74	0.08829	1.91	2.0672	16.91	2.60	9.83	3.98	4.85	5.38	5.39	10.33	38.58	7.75
carbon dioxide	*N*-(4-methoxybenzyl- -idene)-4-*n*-butylaniline	5	3.58462	-763.577	0.24	0.25367	1.77	2.1419	29.00	0.33	42.04	30.23	3.72	17.85	5.56	7.95	47.09	1.84
carbon dioxide	*n*-butylbenzene	15	3.19455	961.172	1.75	0.07994	1.90	1.4109	15.95	2.97	11.18	2.77	16.57	6.29	5.39	5.62	61.07	13.93
carbon dioxide	*tert*-butylbenzene	15	3.47854	354.559	3.02	0.09036	3.87	1.8018	23.59	3.62	9.25	3.26	14.03	7.92	3.35	3.51	56.49	10.83
carbon dioxide	butyric acid ethyl ester	16	3.57333	151.103	1.69	0.08676	3.64	2.2177	27.36	1.89	3.91	3.54	6.58	4.31	2.96	7.13	53.47	11.80
carbon dioxide	caffeine	21	2.28334	2294.191	3.32	0.03340	8.05	0.7164	-17.53	4.87	37.00	6.83	31.48	22.62	36.24	37.03	107.91	47.40
carbon dioxide	capric acid ethyl ester	16	3.53104	65.611	1.26	0.11632	3.85	1.7729	29.09	1.44	10.56	2.88	16.75	13.46	3.77	2.46	64.43	11.25
carbon dioxide	caprylic acid ethyl ester	16	3.51901	186.415	1.48	0.10496	2.93	1.7619	26.83	1.67	7.39	2.45	14.33	10.23	4.14	1.73	62.85	12.15
carbon dioxide	*β*-carotene	90	2.85304	1673.475	1.05	0.10901	1.38	0.6748	16.79	2.26	144.58	8.79	66.19	14.88	20.36	5.82	112.10	33.25
carbon dioxide	L-carvone	27	3.31477	717.257	3.17	0.08177	3.51	1.6464	23.91	2.62	10.97	4.76	24.41	3.66	12.00	12.01	71.52	21.08

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	chlorobenzene	15	2.77704	1778.374	3.03	-0.02258	3.92	1.4476	11.52	3.61	8.91	5.24	12.35	8.22	10.29	21.63	60.41	21.67
carbon dioxide	citral	15	3.41786	370.633	2.66	0.10759	3.19	1.3860	16.29	4.31	10.55	3.50	11.19	8.63	5.29	3.45	63.44	13.20
carbon dioxide	cobalt(III) acetylacetonate	38	3.21002	1386.950	1.37	0.00682	1.59	1.0715	17.87	2.13	125.95	12.44	47.22	11.53	29.97	25.24	104.07	40.06
carbon dioxide	copper(II) trifluoroacetylacetonate	12	3.28343	1692.002	4.46	-0.08244	4.73	1.2764	22.66	5.04	72.60	17.87	52.90	37.09	49.65	53.26	125.99	62.37
carbon dioxide	dibenzo-24-crown-8	28	3.26922	696.407	1.66	0.14589	2.06	1.0944	24.24	1.93	99.02	9.04	51.41	12.73	13.08	2.71	89.14	22.77
carbon dioxide	15-crown-5	29	3.03865	1026.522	4.17	0.14571	5.18	0.9986	1.19	5.98	21.17	13.43	15.09	7.85	12.64	11.20	74.02	21.59
carbon dioxide	cycloheptanone	8	3.54365	376.461	1.60	0.06632	2.95	1.8569	23.71	1.85	8.58	5.33	18.83	24.01	26.38	40.45	83.17	39.72
carbon dioxide	cyclononanone	8	3.49843	469.612	2.21	0.07448	3.25	1.7583	25.46	2.33	10.68	4.12	22.69	17.62	25.13	31.85	86.08	36.52
carbon dioxide	cyclopentanone	8	3.39322	939.686	0.91	0.01800	1.04	1.8382	18.40	1.03	13.18	7.64	9.61	20.31	19.56	37.55	70.71	33.53
carbon dioxide	*n*-decane	5	3.93322	-1936.973	1.49	0.22525	3.70	3.8443	36.48	1.47	32.31	27.51	21.11	38.51	29.10	31.07	10.62	23.56
carbon dioxide	dibenzyl ether	15	2.98169	1625.220	1.80	0.05144	2.14	1.0702	14.04	3.22	15.81	5.56	38.16	5.32	20.72	17.22	88.51	30.14
carbon dioxide	1,2-dichlorobenzene	15	3.12601	1152.511	1.17	0.08502	1.48	1.5427	16.61	2.07	10.51	9.25	17.55	6.89	11.69	19.05	65.11	22.17
carbon dioxide	*p*-dichlorobenzene	13	3.20761	1101.195	3.32	0.06711	3.54	1.5067	16.27	3.72	8.76	8.46	17.02	10.61	16.00	24.31	71.04	27.05
carbon dioxide	diethyl ether	15	2.10746	2151.564	8.81	-0.02103	16.55	1.0474	-26.59	4.98	32.29	6.98	9.09	11.80	12.38	24.74	59.29	22.80
carbon dioxide	1,2-diethylbenzene	15	3.14091	1078.383	1.66	0.07677	1.79	1.3663	15.06	2.61	11.78	3.30	17.28	6.19	6.01	6.09	61.99	14.43
carbon dioxide	1,4-diethylbenzene	15	3.41019	503.929	2.47	0.07720	2.98	1.3865	15.72	4.06	11.17	3.56	18.05	5.65	6.72	6.97	63.10	15.36
carbon dioxide	diisopropyl ether	15	2.71160	1475.518	6.90	0.03391	12.60	1.0782	-16.29	7.87	29.92	8.47	11.51	7.14	6.46	9.41	52.65	12.53
carbon dioxide	2,3-dimethylaniline	15	3.13116	1483.496	2.01	0.01766	1.95	1.2259	13.77	2.38	12.08	16.97	33.42	16.04	24.54	29.92	86.17	35.59
carbon dioxide	2,6-dimethylaniline	15	2.96718	1763.082	2.05	0.02213	2.66	1.1330	8.66	3.34	11.78	12.35	28.06	11.47	19.64	24.80	78.84	30.25
carbon dioxide	1,1'-dimethylferrocene	68	3.30367	983.373	2.28	0.04437	2.78	1.2835	11.85	3.67	29.12	17.13	18.70	12.16	20.35	25.53	79.91	31.02

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}··s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	2,6-dimethylnaphthalene	6	3.14389	1042.020	3.71	0.09742	3.84	1.1736	10.78	4.24	15.38	5.28	18.68	7.15	9.26	8.88	67.76	17.98
carbon dioxide	2,7-dimethylnaphthalene	6	3.22622	950.709	4.32	0.09184	4.35	1.5069	19.63	4.50	11.91	4.68	16.04	6.91	6.00	5.64	60.69	13.01
carbon dioxide	2,4-dimethylphenol	15	2.88913	1876.681	2.13	0.02223	2.58	1.1649	8.33	3.63	11.95	8.03	24.55	9.42	16.90	22.58	74.26	27.40
carbon dioxide	diolein	9	2.82785	1404.144	1.26	0.12451	1.64	0.6769	14.02	1.61	77.97	4.84	48.58	23.69	9.91	5.27	95.83	22.33
carbon dioxide	1,3-divinylbenzene	15	3.13705	1037.564	1.00	0.08850	1.09	1.5589	18.35	1.39	12.10	2.34	16.58	3.74	7.74	10.19	62.36	16.70
carbon dioxide	docosahexaenoic acid (DHA)	63	3.02798	1295.914	1.23	0.10524	1.38	0.9163	18.60	1.63	58.53	9.19	48.35	7.28	19.86	8.29	100.02	30.05
carbon dioxide	DHA ethyl ester	65	3.20656	755.350	0.93	0.13878	2.28	1.0708	22.09	1.45	48.46	1.67	31.39	16.73	9.27	2.00	84.14	18.88
carbon dioxide	DHA methyl ester	17	3.31563	486.177	0.72	0.13998	2.99	1.2079	25.70	0.92	52.38	2.34	32.12	16.76	8.37	2.47	81.78	17.74
carbon dioxide	*n*-dodecane	5	4.09753	-2726.468	2.97	0.25928	5.39	4.3507	39.93	2.99	37.54	29.20	19.59	40.87	29.79	33.31	11.47	24.36
carbon dioxide	eicosapentaenoic acid (EPA)	55	2.94303	1358.327	1.06	0.11480	1.20	0.9184	16.15	1.79	46.01	7.35	41.67	7.79	17.55	7.30	94.51	27.28
carbon dioxide	EPA ethyl ester	48	3.29202	588.218	0.63	0.13391	2.80	1.1626	24.23	1.06	36.48	1.55	29.92	14.98	10.14	1.02	84.21	19.58
carbon dioxide	EPA methyl ester	17	3.40465	360.554	0.41	0.12124	3.62	1.2964	27.43	0.49	37.76	1.65	30.48	17.37	7.27	3.34	79.62	16.49
carbon dioxide	ethanol	24	3.14518	962.021	2.80	0.18276	3.00	1.9621	6.43	3.21	12.41	4.48	9.68	11.29	5.39	32.94	39.86	19.52
carbon dioxide	ethyl acetate	15	2.19717	2093.221	12.09	0.01721	19.64	0.8254	-49.61	6.71	36.32	8.62	8.21	12.75	13.77	26.10	62.20	24.58
carbon dioxide	ethylbenzene	15	3.36152	499.393	1.51	0.09142	2.07	1.8248	18.85	2.28	9.47	4.72	4.84	7.44	3.41	4.76	46.77	7.97
carbon dioxide	ethyl benzoate	15	3.64711	-213.004	2.61	0.07820	4.93	1.8993	27.23	2.94	12.20	4.95	24.86	3.88	12.77	13.39	72.14	22.01
carbon dioxide	ethylene	48	2.35702	1633.913	3.62	-0.04759	5.18	2.9026	-3.87	4.79	9.12	—	—	—	—	—	—	—
carbon dioxide	2-ethyltoluene	15	2.92765	1398.686	2.94	0.07787	3.28	1.4172	14.72	3.76	9.30	5.62	10.53	8.95	4.63	4.63	53.63	9.76
carbon dioxide	3-ethyltoluene	15	3.06313	1193.724	3.38	0.07505	3.59	1.4175	14.91	4.00	9.82	6.07	9.09	11.68	5.28	5.07	50.98	7.07
carbon dioxide	4-ethyltoluene	15	3.02453	1318.582	2.49	0.06181	2.68	1.4780	17.40	3.07	8.89	8.12	12.72	7.46	4.10	4.86	56.37	11.41

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	eugenol	15	3.49489	730.482	2.42	0.02183	3.36	1.3885	20.62	3.58	10.54	7.33	39.69	17.29	28.35	31.11	94.09	39.19
carbon dioxide	ferrocene	107	3.17659	675.060	3.51	0.15686	4.35	1.2243	5.68	6.96	21.29	19.84	17.31	17.43	21.04	32.55	76.62	33.28
carbon dioxide	2-fluoroanisole	15	3.01339	1523.346	1.43	0.04081	1.66	1.3944	14.19	2.58	9.93	3.35	26.66	18.48	22.85	33.51	79.91	35.01
carbon dioxide	fluorobenzene	15	3.29841	1010.407	3.54	0.02651	3.64	1.7808	17.76	4.22	10.40	4.34	10.83	11.04	11.16	26.57	59.41	23.76
carbon dioxide	helium	56	3.35817	103.962	0.88	-0.01597	0.88	16.6246	3737.63	1.23	69.32	–	–	–	–	–	–	–
carbon dioxide	*n*-heptane	5	3.96390	-1674.975	1.03	0.17552	3.31	3.9421	35.67	1.00	20.99	19.03	18.71	28.91	22.68	20.51	16.50	16.05
carbon dioxide	2-heptanone	11	3.38664	-142.202	3.79	0.20302	4.47	3.4792	32.29	1.83	22.02	26.86	23.07	30.11	24.33	21.82	13.71	17.77
carbon dioxide	4-heptanone	9	3.63051	-1022.393	0.46	0.25169	2.19	3.1752	27.31	0.47	29.62	32.43	29.68	36.53	30.93	29.03	4.11	25.01
carbon dioxide	hexachlorobenzene	14	2.53070	1519.423	2.94	0.15688	7.77	0.8331	-12.47	4.18	25.04	25.68	14.18	10.99	13.01	12.63	71.35	20.34
carbon dioxide	1-hexadecene	11	2.61695	1721.477	9.36	0.08567	11.13	0.7329	-8.63	11.75	35.05	10.01	21.13	16.17	11.89	10.73	76.80	18.73
carbon dioxide	1,1,1,5,5,5- -hexafluoroacetylacetone	15	3.16949	1277.236	3.85	0.03641	4.08	1.1460	11.05	4.36	23.39	10.10	32.24	18.95	27.98	33.14	91.59	39.26
carbon dioxide	*n*-hexane	5	3.90162	-1233.726	1.85	0.14894	2.85	3.9838	35.55	2.09	16.06	14.11	16.44	22.91	18.40	13.51	20.98	10.85
carbon dioxide	hydrogen	7	2.81422	429.524	0.27	-0.03864	0.38	19.8027	5898.70	0.28	73.95	–	–	–	–	–	–	–
carbon dioxide	iodobenzene	15	2.87494	1790.731	2.53	0.05395	3.28	1.2680	11.18	2.72	11.69	16.88	22.56	12.21	17.69	26.12	73.53	28.89
carbon dioxide	D-limonene	15	3.00743	1114.287	2.61	0.10763	3.15	1.3735	12.04	4.06	10.49	4.03	7.22	9.32	4.27	4.20	57.32	10.54
carbon dioxide	linalool	15	3.17484	975.465	3.14	0.08351	3.49	1.3508	14.09	4.02	11.26	3.52	10.49	7.24	5.63	4.13	63.29	13.86
carbon dioxide	linoleic acid	71	2.79398	1722.115	2.00	0.07315	3.25	0.8351	9.74	3.73	30.68	7.14	38.00	9.63	15.88	7.28	90.41	25.29
carbon dioxide	linoleic acid methyl ester	21	2.96798	1273.700	1.41	0.10941	1.40	1.0645	19.77	1.66	56.92	2.11	37.24	15.74	7.44	3.30	77.97	16.35
carbon dioxide	α-linolenic acid	56	2.93438	1495.139	1.29	0.07553	1.83	0.9745	15.74	2.79	26.31	5.15	32.29	14.24	9.32	4.65	81.08	18.39
carbon dioxide	γ-linolenic acid	142	2.76744	1549.053	1.37	0.11542	2.79	0.8364	9.15	2.15	33.37	7.90	36.36	7.79	16.90	8.37	92.13	26.40

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	γ-linolenic acid ethyl ester	41	2.85726	1364.347	4.03	0.09357	6.27	0.8603	6.15	5.10	43.72	9.79	23.99	6.92	27.87	19.79	105.41	37.84
carbon dioxide	γ-linolenic acid methyl ester	52	3.11417	955.354	4.27	0.11043	5.39	0.8588	7.53	7.58	47.11	6.85	19.94	13.41	10.20	4.68	82.00	19.17
carbon dioxide	L-menthone	23	3.40931	450.747	3.24	0.09705	4.05	1.7676	25.22	2.81	11.73	3.65	19.79	5.18	7.36	6.71	65.04	15.93
carbon dioxide	methanol	10	2.22609	2302.163	2.09	0.08572	3.90	2.1980	1.60	2.14	20.87	6.17	18.17	16.79	7.10	46.84	33.18	23.92
carbon dioxide	2-methylanisole	15	3.13154	1273.877	1.78	0.04705	1.99	1.3055	12.12	2.79	9.69	5.18	22.89	9.67	16.19	23.02	72.34	26.90
carbon dioxide	4-methylanisole	15	3.34952	1039.036	1.86	0.01437	2.41	1.3473	16.11	3.21	12.16	12.63	31.81	17.52	24.50	31.83	84.67	35.98
carbon dioxide	1-methylnaphthalene	11	2.62663	2165.127	5.22	0.00072	10.02	0.7415	-17.13	6.64	37.94	19.06	29.56	20.35	30.86	32.73	98.69	41.75
carbon dioxide	monoolein	11	2.93202	1551.866	0.95	0.07217	1.40	0.8199	13.88	1.22	24.17	5.13	43.52	8.71	18.90	7.31	99.51	29.20
carbon dioxide	myristic acid ethyl ester	16	3.48694	108.431	2.00	0.13220	3.84	1.4546	27.11	2.14	24.88	3.07	23.65	15.97	4.92	3.60	71.66	13.35
carbon dioxide	myristoleic acid	42	2.71934	1634.443	1.48	0.08701	4.06	0.8465	4.77	2.66	25.97	13.91	31.43	5.68	22.90	14.76	98.00	32.51
carbon dioxide	myristoleic acid methyl ester	79	2.19213	1721.828	7.68	0.04059	9.85	0.7247	-15.38	10.07	68.29	11.93	14.33	10.41	19.80	13.01	94.13	29.12
carbon dioxide	naphthalene	112	2.97988	1192.296	8.67	0.12057	10.14	1.1749	0.32	9.86	19.36	11.49	9.31	10.87	10.33	10.94	53.66	13.53
carbon dioxide	1-naphthol	11	3.57490	36.077	0.38	0.15453	2.18	2.1460	24.53	0.88	9.22	18.59	4.60	5.77	0.39	5.67	48.49	9.17
carbon dioxide	2-naphthol	16	3.59573	-20.532	0.52	0.16301	2.53	1.9948	21.27	1.73	6.52	23.33	10.71	7.84	2.46	5.02	45.23	7.67
carbon dioxide	2-nitroanisole	15	3.14470	1347.654	1.44	0.05278	1.63	1.2984	15.75	2.39	10.88	3.48	30.58	11.47	20.75	24.69	81.49	31.20
carbon dioxide	nitrobenzene	15	3.13306	1252.325	1.94	0.06177	2.17	1.2975	9.79	3.33	9.96	4.21	19.22	8.79	13.98	22.29	67.96	24.87
carbon dioxide	3-nitrotoluene	15	3.31886	846.963	2.31	0.06904	2.74	1.3849	14.90	3.96	9.58	2.86	18.41	4.00	8.67	11.30	64.09	17.91
carbon dioxide	*n*-nonane	5	4.05719	-2321.942	1.42	0.22243	3.65	4.0604	37.02	1.43	29.33	25.69	21.11	36.45	27.94	28.90	11.31	22.22
carbon dioxide	2-nonanone	10	3.61751	-917.672	2.29	0.25191	4.21	2.8331	29.00	2.35	25.05	29.36	25.20	35.76	27.22	28.14	12.37	21.43
carbon dioxide	5-nonanone	12	3.77309	-1266.610	1.10	0.23313	4.95	3.0575	32.15	1.10	25.83	26.31	20.80	34.31	25.24	26.49	15.74	19.33

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*n*-octane	5	4.04732	-2166.543	1.58	0.20281	3.65	4.1527	37.05	1.66	25.60	22.91	20.36	33.41	25.91	25.59	13.16	19.86
carbon dioxide	oleic acid	19	2.84657	1685.151	1.43	0.07040	2.52	0.8088	9.94	2.14	37.36	7.78	40.02	10.03	16.61	7.86	91.81	26.11
carbon dioxide	oleic acid ethyl ester	5	2.12604	1755.563	1.18	0.05356	5.87	0.5458	-23.03	0.97	53.72	5.13	29.14	5.72	27.68	16.67	113.19	38.56
carbon dioxide	oleic acid methyl ester	19	2.37496	1745.194	3.08	0.01920	8.59	0.5031	-34.23	1.93	65.15	6.26	27.79	6.50	31.10	19.06	117.76	42.07
carbon dioxide	palladium(II) acetylacetonate	125	3.22614	1388.277	2.34	0.02298	2.86	1.2460	17.11	4.65	91.51	18.95	38.05	21.93	32.80	36.33	100.26	44.15
carbon dioxide	palmitic acid ethyl ester	17	3.37638	396.044	0.57	0.12236	3.18	1.3142	26.47	0.61	30.82	1.46	28.90	15.14	8.02	1.75	78.79	16.97
carbon dioxide	*n*-pentane	5	3.99545	-1437.031	1.52	0.09652	3.15	4.0586	35.82	1.67	9.12	6.62	12.10	13.23	11.26	2.49	28.89	2.52
carbon dioxide	2-pentanone	23	3.27060	600.626	1.95	0.09926	2.06	1.7185	12.62	2.52	7.78	4.35	2.27	4.45	4.27	13.04	47.94	12.64
carbon dioxide	3-pentanone	39	3.28340	577.407	1.57	0.09769	1.72	2.0419	19.27	2.03	9.03	4.22	4.31	9.48	6.20	3.73	38.28	4.37
carbon dioxide	2,4-dimethyl-3-pentanone	8	3.52819	623.504	2.21	0.01519	3.25	1.7583	25.46	2.33	24.76	15.38	19.64	11.25	20.20	24.47	80.41	30.68
carbon dioxide	2,2,4,4-tetramethyl-3-pentanone	9	3.68923	-957.980	0.70	0.23527	2.92	3.0352	29.08	0.76	24.62	33.00	20.80	27.01	21.41	18.31	17.70	14.50
carbon dioxide	*n*-pentylbenzene	31	3.23258	876.323	1.77	0.08163	2.04	1.6182	21.86	3.86	12.91	3.85	17.17	8.38	5.24	4.20	62.41	13.44
carbon dioxide	phenanthrene	19	2.73481	1181.959	4.40	0.17684	5.49	1.3448	12.04	5.03	23.94	13.72	6.02	13.96	7.78	8.06	51.15	8.79
carbon dioxide	phenol	109	3.15615	1134.915	2.89	0.06926	3.12	1.3527	2.15	4.66	7.84	5.30	10.36	21.20	17.97	39.93	66.34	33.07
carbon dioxide	phenylacetic acid	16	3.35377	734.319	1.47	0.08843	2.01	1.7122	22.71	1.80	6.41	1.62	15.84	4.25	12.95	16.60	69.79	22.72
carbon dioxide	phenylacetylene	15	3.21540	1124.472	1.09	0.04421	1.22	1.6377	17.26	1.58	7.61	4.46	16.04	7.80	12.00	21.03	64.46	22.91
carbon dioxide	1-phenyldodecane	15	3.13079	1395.126	1.88	0.02988	2.37	0.9485	17.21	3.14	26.54	16.09	47.18	6.96	18.09	7.99	94.23	27.70
carbon dioxide	1-phenylethanol	15	3.22841	1266.644	1.60	0.02205	1.84	1.3428	14.22	3.15	11.15	7.66	25.33	10.31	17.97	23.56	75.96	28.54
carbon dioxide	2-phenylethanol	15	3.13278	1425.565	1.68	0.02656	2.00	1.3652	15.18	3.03	10.31	8.49	26.79	12.10	19.59	25.60	78.14	30.39
carbon dioxide	2-phenylethyl acetate	15	2.98823	1723.798	1.52	0.02441	2.09	1.1080	13.22	3.06	13.89	9.82	36.37	8.63	22.22	21.45	87.91	32.02

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}··s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	1-phenylhexane	15	3.11637	1162.079	1.81	0.07294	1.95	1.2534	16.08	2.71	14.59	4.98	23.78	7.52	7.80	5.06	68.63	16.20
carbon dioxide	phenylmethanol	15	3.31015	954.535	1.58	0.04883	1.79	1.5257	16.57	2.54	8.05	7.02	22.63	13.91	18.50	28.26	73.87	30.10
carbon dioxide	1-phenyloctane	15	2.99987	1340.955	2.32	0.08161	2.57	1.1894	16.53	3.65	20.79	3.77	27.35	8.65	8.49	3.91	72.00	16.88
carbon dioxide	3-phenylpropyl acetate	15	2.86639	1916.569	1.78	0.02311	2.56	1.0565	12.96	3.37	14.86	9.79	38.05	7.12	21.63	18.93	89.00	31.18
carbon dioxide	*α*-pinene	15	3.46812	373.899	3.03	0.09860	3.61	1.7055	21.73	3.83	9.38	4.11	9.28	7.00	4.66	4.68	59.39	12.54
carbon dioxide	*β*-pinene	15	3.18082	723.286	3.43	0.12156	3.59	1.3716	9.22	4.97	10.14	6.66	5.08	11.72	4.07	4.08	51.21	7.30
carbon dioxide	2-phenyl-1-propanol	15	3.18377	1454.329	1.51	0.00374	1.73	1.2825	15.24	2.64	15.83	9.53	30.05	9.72	19.88	22.66	81.11	30.05
carbon dioxide	3-phenyl-1-propanol	15	3.42174	830.704	1.60	0.02829	2.17	1.5158	20.64	2.28	9.50	7.82	27.20	6.21	16.54	18.65	76.57	26.32
carbon dioxide	1-propanol	17	2.60954	1787.578	3.00	0.24133	4.99	1.3448	-10.04	3.00	8.71	10.36	4.49	15.43	11.60	33.81	56.46	26.25
carbon dioxide	2-propanol	18	2.32678	1835.914	2.19	0.06695	3.97	1.5735	-1.37	2.21	7.42	6.43	7.64	9.57	6.96	26.96	48.70	19.89
carbon dioxide	*i*-propylbenzene	15	3.22089	813.642	2.09	0.09346	2.23	1.6274	17.00	2.00	10.94	4.82	7.33	9.27	4.11	4.28	49.12	7.60
carbon dioxide	*n*-propylbenzene	34	2.49520	1842.078	4.35	0.07363	9.46	0.8647	-17.49	5.03	25.18	8.65	8.67	12.75	14.62	15.88	66.76	20.46
carbon dioxide	pyrene	18	3.44041	215.609	0.71	0.13834	4.17	1.5497	23.47	1.84	26.23	6.84	20.83	9.18	5.95	2.73	65.38	13.72
carbon dioxide	squalene	5	3.94121	-1154.877	1.62	0.12635	4.89	1.9069	36.68	1.87	50.04	10.81	38.21	13.56	11.21	3.78	85.24	20.60
carbon dioxide	stearic acid ethyl ester	17	3.36937	413.011	0.71	0.12763	3.45	1.2474	26.37	1.03	41.53	1.65	31.65	16.25	8.48	2.16	81.42	17.77
carbon dioxide	styrene	15	3.07797	1398.876	3.94	0.03774	4.10	1.6454	18.93	4.39	8.35	9.17	14.72	5.38	9.91	17.70	62.10	20.35
carbon dioxide	*n*-tetradecane	5	4.13929	-2995.159	3.07	0.24688	7.77	4.3703	41.99	3.32	43.05	25.26	12.24	38.78	25.35	30.40	20.42	19.50
carbon dioxide	tetrahydrofuran	15	2.04981	2291.940	7.86	0.01551	14.70	1.1871	-22.18	4.99	22.16	8.80	10.90	15.96	12.43	34.15	58.17	27.07
carbon dioxide	thenoyltrifluoroacetone	15	3.14095	1255.100	3.02	0.07265	3.09	1.1938	18.09	3.06	13.70	4.04	47.64	30.20	41.38	45.60	112.83	53.55
carbon dioxide	*α*-tocopherol	82	2.98271	1251.498	1.10	0.12003	1.32	0.9419	18.16	2.21	64.17	9.43	27.17	31.55	5.63	16.48	65.05	4.98

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	toluene	35	3.44756	387.021	3.72	0.05873	4.29	1.6490	11.47	4.14	8.44	5.43	4.46	5.32	5.03	11.33	48.08	11.84
carbon dioxide	triarachidonin	27	2.64208	1932.081	0.49	0.12016	3.16	0.4912	6.85	0.82	149.21	10.98	70.26	17.49	20.63	8.39	116.86	34.89
carbon dioxide	trierucin	101	2.49650	2090.808	1.57	0.09500	4.99	0.3731	-2.73	2.95	146.62	7.37	82.31	13.57	31.19	14.68	140.57	48.33
carbon dioxide	trifluoroacetylacetone	15	3.34985	655.314	1.73	0.09124	1.82	1.7229	19.57	2.18	6.36	14.09	11.17	3.74	9.06	15.88	61.49	19.21
carbon dioxide	1,3,5-trimethylbenzene	24	2.86058	1615.576	3.77	0.04718	4.47	1.2531	11.01	4.29	13.33	10.57	19.18	7.27	14.10	16.95	71.51	23.55
carbon dioxide	trinervonin	38	2.56082	2040.567	1.46	0.10235	4.11	0.3962	2.77	2.86	163.95	6.58	83.21	16.62	27.91	12.12	136.63	45.38
carbon dioxide	triolein	10	2.61414	1511.306	0.89	0.17644	3.48	0.4442	-1.58	1.26	139.27	5.95	53.87	26.03	13.52	6.04	110.08	29.06
carbon dioxide	ubiquinone CoQ10	80	2.84521	1753.851	2.21	0.10423	2.69	0.6220	16.09	4.09	141.53	7.87	71.55	13.90	23.98	8.60	120.85	37.98
carbon dioxide	*n*-undecane	5	3.99263	-2282.843	1.88	0.24395	4.47	4.1553	38.28	1.85	35.87	29.69	21.81	40.94	30.82	33.61	8.96	25.46
carbon dioxide	6-undecanone	13	3.67662	-1037.914	2.16	0.24323	4.89	2.8101	31.76	2.53	27.81	28.03	19.58	36.53	25.70	28.65	16.98	19.94
carbon dioxide	vanillin	15	3.31967	996.088	1.74	0.05836	1.92	1.5345	21.13	2.03	10.92	2.63	24.63	12.64	21.65	26.02	82.53	32.26
carbon dioxide	vitamin K$_1$	16	2.88651	1097.764	1.99	0.19147	2.15	0.8940	16.80	2.22	106.89	9.99	30.62	27.19	4.19	11.84	72.64	9.60
carbon dioxide	vitamin K$_3$	20	2.95781	1094.816	1.88	0.15361	3.69	1.1807	8.84	2.70	24.21	8.88	11.31	9.77	7.48	7.14	61.05	12.90
carbon dioxide	water	24	3.88157	-887.370	4.05	-0.12782	13.05	8.3239	36.48	4.18	25.10	25.73	13.26	56.20	19.65	128.05	23.60	69.13
carbon dioxide	*m*-xylene	12	2.38098	2322.960	13.08	0.01369	20.09	0.7183	-34.12	10.53	52.18	14.94	16.46	17.73	23.95	30.75	83.81	35.11
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	3.32414	679.927	1.75	0.08363	2.26	1.5998	22.80	3.10	13.66	3.32	19.40	8.49	5.79	3.60	64.71	14.06
carbon monoxide	helium	7	2.86105	271.537	0.13	0.06392	0.21	22.1377	5018.43	0.16	69.03	—	—	—	—	—	—	—
carbon monoxide	hydrogen	7	3.10490	206.278	0.13	-0.00012	0.20	22.1377	5018.43	0.16	70.85	—	—	—	—	—	—	—
chlorotrifluoromethane	acetone	10	2.71928	3047.636	2.39	-0.14547	5.96	0.9096	19.58	2.56	5.85	8.40	—	23.27	29.79	23.24	25.58	25.58
chlorotrifluoromethane	1,3-dibromobenzene	12	3.37195	2729.504	5.75	-0.09328	9.07	0.4102	-5.89	6.09	58.10	12.65	—	46.23	27.38	36.57	77.72	28.76

Table 1 (*Continued*)

System			New Model			TLSM$_\mathrm{d}$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{\mathrm{LJ},1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,\mathrm{d}}$	AARD	$B \times 10^7$ (mol·cm^{-1}· ·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
chlorotrifluoromethane	*p*-xylene	8	2.18818	3426.492	3.22	-0.12185	11.82	0.4851	-13.32	2.28	38.21	7.10	—	23.77	22.00	21.70	39.07	21.94
cyclohexane	argon	6	5.63584	621.560	1.67	0.07877	10.21	2.6698	96.95	2.44	43.30	—	—	21.29	36.48	49.69	55.63	4.19
cyclohexane	benzene	12	5.64658	1187.885	2.66	0.01052	6.07	1.4520	101.34	3.04	66.34	—	—	25.76	25.74	31.11	26.54	25.21
cyclohexane	carbon tetrachloride	6	5.62964	1465.504	1.09	0.05711	3.02	1.3613	102.47	1.11	71.72	—	—	6.41	5.52	26.29	10.65	4.69
cyclohexane	1,1'-dimethylferrocene	5	5.64091	2497.057	5.02	-0.12263	5.08	0.5416	98.23	5.36	219.79	—	—	28.45	39.02	61.84	36.11	37.44
cyclohexane	ethane	5	5.60416	1335.180	1.24	0.01358	10.22	2.0214	100.00	2.40	106.17	—	—	25.57	32.30	17.02	49.22	17.12
cyclohexane	ethylene	5	5.58406	1498.158	0.80	-0.00840	10.85	2.1435	99.75	2.30	102.01	—	—	25.19	33.48	21.04	50.76	15.54
cyclohexane	ethylferrocene	6	5.61637	2647.319	4.27	-0.10469	4.39	0.5775	99.11	5.21	191.79	—	—	29.02	39.63	62.55	36.71	38.05
cyclohexane	ferrocene	5	5.63794	1973.289	5.02	0.00232	5.27	0.5481	97.15	5.52	71.03	—	—	35.44	40.75	77.76	34.52	44.73
cyclohexane	krypton	6	5.60647	1608.126	0.99	0.06555	10.23	2.1405	98.04	1.26	66.64	—	—	8.49	23.56	63.83	45.50	9.36
cyclohexane	methane	6	5.61427	1266.094	0.59	-0.09598	7.38	2.8585	99.81	0.68	40.39	—	—	28.46	39.35	24.92	56.38	16.26
cyclohexane	naphthalene	12	5.63646	1341.724	1.89	0.07176	7.66	1.1611	101.24	2.99	40.63	—	—	26.63	24.44	23.86	24.66	24.61
cyclohexane	phenanthrene	8	5.62921	1271.924	1.46	0.06355	6.30	0.9775	101.00	4.31	6.34	—	—	39.49	30.69	27.25	29.80	34.47
cyclohexane	tetrabutyltin	7	5.63744	2054.433	1.85	0.00126	2.48	0.7438	103.12	2.35	13.61	—	—	6.48	16.43	12.44	21.90	8.50
cyclohexane	tetraethyltin	7	5.63947	1540.947	1.46	0.05902	2.90	1.0441	102.93	2.16	57.13	—	—	5.80	7.45	20.03	6.75	6.36
cyclohexane	tetramethyltin	7	5.61319	1704.528	1.36	0.06161	4.55	1.2553	102.25	1.25	94.10	—	—	4.80	5.16	40.13	3.53	10.31
cyclohexane	tetrapropyltin	6	5.63657	1781.608	1.06	0.03986	3.08	0.8573	102.94	2.10	21.82	—	—	4.89	12.46	14.79	14.08	7.53
cyclohexane	toluene	12	5.62964	1303.314	1.86	0.04098	7.90	1.3305	100.99	2.85	55.83	—	—	26.14	24.81	24.36	26.52	24.07
cyclohexane	1,3,5-trimethylbenzene	12	5.63009	1472.492	2.27	0.04290	6.82	1.1194	101.54	2.42	56.15	—	—	26.15	24.79	24.87	24.90	24.98
cyclohexane	xenon	6	5.50370	2017.999	1.05	0.06313	9.40	1.8186	99.39	1.15	85.28	—	—	5.62	15.35	60.65	37.97	13.76

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
cyclohexane	*p*-xylene	8	5.60180	1333.319	1.06	0.02861	7.62	1.2210	100.22	3.88	28.73	—	—	40.98	36.75	24.95	38.43	36.91
deuterium	hydrogen	5	2.40960	1.996	2.81	0.07325	2.10	34.7676	2840.99	1.14	35.80	—	—	—	—	—	—	—
2,3-dimethylbutane	benzene	11	5.52708	1336.166	1.28	-0.03830	1.65	0.9661	70.08	1.56	7.93	4.46	—	75.95	81.84	156.21	56.59	95.80
2,3-dimethylbutane	naphthalene	9	5.46162	1575.646	1.15	0.01329	2.07	0.7527	66.74	1.75	2.41	2.76	—	65.82	85.96	119.78	68.14	82.61
2,3-dimethylbutane	phenanthrene	11	5.18117	1947.218	1.02	0.04521	2.91	0.5871	54.23	1.53	5.23	2.49	—	61.35	90.49	104.02	77.61	78.84
2,3-dimethylbutane	toluene	10	5.68693	1046.194	1.27	-0.02904	1.41	0.9458	77.91	1.79	4.82	4.74	—	72.49	84.58	140.62	62.29	90.48
n-dodecane	acetone	5	6.99253	1854.245	1.13	-0.14932	1.17	0.8244	215.52	1.68	102.53	—	—	16.62	3.20	86.12	34.68	23.08
n-dodecane	carbon dioxide	9	6.94566	2070.237	1.17	-0.09410	9.67	1.2167	210.03	2.20	23.83	—	—	10.06	30.15	93.72	58.09	18.79
n-dodecane	carbon monoxide	9	6.79625	2805.495	4.81	-0.23411	9.34	1.4392	212.70	5.90	27.26	—	—	17.45	38.00	72.63	62.82	16.32
n-dodecane	*n*-decane	5	6.90537	2096.686	1.74	-0.03191	2.18	0.5822	219.24	2.98	29.97	—	—	21.54	18.92	12.00	30.49	25.19
n-dodecane	*n*-hexadecane	5	6.90931	2621.223	2.49	0.08490	4.43	0.4466	221.99	6.69	19.30	—	—	14.84	12.56	12.69	14.84	19.00
n-dodecane	hydrogen	9	6.90833	3760.817	4.31	-0.73235	6.29	3.9660	215.14	5.29	47.80	—	—	59.75	71.88	13.38	83.78	44.93
n-dodecane	naphthalene	5	6.93350	2108.119	1.51	-0.01689	1.77	0.5064	214.04	1.41	81.24	—	—	12.27	8.59	48.57	23.94	9.28
n-dodecane	*n*-octane	9	6.92934	1782.639	1.32	-0.02986	1.47	0.6640	218.97	1.48	25.45	—	—	21.35	21.56	12.11	34.17	24.34
n-dodecane	*n*-tetradecane	5	6.85746	2568.929	2.45	-0.04059	3.70	0.4729	221.14	7.84	17.19	—	—	18.00	15.58	15.38	19.31	20.79
n-eicosane	carbon dioxide	5	8.29717	3272.226	1.41	-0.23808	4.71	0.8724	352.03	2.07	21.16	—	—	16.80	37.40	108.39	64.95	21.39
n-eicosane	carbon monoxide	5	8.30012	3426.107	1.79	-0.36820	2.88	1.0324	354.30	2.43	31.74	—	—	19.36	44.76	84.64	69.09	15.23
n-eicosane	*n*-dodecane	5	8.16282	3551.406	1.79	-0.18043	2.29	0.3222	361.84	4.28	60.70	—	—	14.60	18.07	8.99	43.31	25.27
n-eicosane	*n*-hexadecane	5	8.14332	3846.104	2.26	-0.06732	2.23	0.2678	362.04	3.44	55.72	—	—	13.47	13.51	9.14	26.38	24.58
n-eicosane	hydrogen	5	8.14387	5975.164	1.92	-0.94563	3.44	3.0212	357.65	4.65	36.80	—	—	62.00	76.22	13.99	87.20	45.86

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}··s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-eicosane	*n*-octane	5	8.13891	3460.435	2.44	-0.22864	3.11	0.4003	359.67	4.78	56.15	—	—	16.80	25.59	12.53	50.47	24.94
ethane	helium	7	4.28973	20.967	0.05	-0.01178	0.17	13.8400	3332.91	0.12	66.86	—	—	—	—	—	—	—
ethane	nitrogen	14	4.40600	399.592	0.97	-0.04068	1.05	4.8313	6847.25	0.95	11.79	—	—	—	—	—	—	—
ethane	1-octene	6	3.54949	1487.006	2.79	0.06902	5.98	1.2050	12.75	1.40	11.82	4.02	—	4.78	50.84	55.22	41.98	54.05
ethane	1-tetradecene	9	3.77571	964.501	1.68	0.13806	2.02	1.5925	38.24	1.61	18.87	7.84	—	17.61	37.74	26.61	37.54	37.37
ethylene	carbon dioxide	49	3.44112	1199.948	3.70	-0.00496	7.27	3.0975	5.29	3.53	9.95	—	—	—	—	—	—	—
ethylene	helium	7	4.05781	34.383	0.07	0.00006	0.08	15.1172	3528.33	0.13	65.75	—	—	—	—	—	—	—
ethylene	nitrogen	7	4.28664	289.435	0.39	-0.03156	0.39	5.0043	5395.35	0.38	8.64	—	—	—	—	—	—	—
helium	argon	36	2.55037	127.780	1.18	0.05432	1.44	19.8282	1030.49	80.41	5.13	—	—	—	—	—	—	—
helium	*n*-butane	19	3.44370	120.396	2.39	-0.07170	2.15	9.7814	3933.52	2.25	81.94	—	—	—	—	—	—	—
helium	*n*-butanol	6	3.16459	196.853	0.71	-0.04352	0.74	9.7503	5049.54	0.75	80.36	—	—	—	—	—	—	—
helium	carbon dioxide	24	3.14937	-6.930	1.01	-0.00665	1.11	14.9552	108.72	8.17	15.22	—	—	—	—	—	—	—
helium	ethane	38	3.09941	105.441	1.14	-0.02441	1.14	14.5940	5284.45	1.63	38.26	—	—	—	—	—	—	—
helium	ethanol	7	3.57462	-612.395	1.20	0.02068	2.62	11.4979	3.23	1.67	39.20	—	—	—	—	—	—	—
helium	ethylene	20	3.44370	-202.340	1.37	-0.01598	1.56	13.5079	1368.22	1.29	31.81	—	—	—	—	—	—	—
helium	*n*-hexane	5	2.83403	621.444	3.54	-0.07133	5.49	9.8844	8733.50	4.76	107.32	—	—	—	—	—	—	—
helium	1-hexanol	6	2.69450	1032.665	0.99	-0.09857	1.42	8.9878	9947.60	1.17	119.99	—	—	—	—	—	—	—
helium	krypton	10	3.00661	213.823	0.70	-0.02154	1.56	21.5512	8054.04	2.59	9.40	—	—	—	—	—	—	—
helium	methane	53	2.86212	65.257	2.86	0.01799	2.39	16.5187	193.60	49.34	16.31	—	—	—	—	—	—	—
helium	methanol	6	2.81299	-154.487	0.83	0.05662	0.94	17.3833	5475.45	0.93	10.56	—	—	—	—	—	—	—

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
helium	nitrogen	34	2.75894	69.095	2.04	0.02849	1.98	18.4724	1099.42	68.90	6.37	–	–	–	–	–	–	–
helium	oxygen	12	2.79145	60.291	1.42	0.03002	1.44	20.8352	4125.27	1.41	2.68	–	–	–	–	–	–	–
helium	1-pentanol	6	2.98831	732.988	1.12	-0.09724	1.19	8.8701	7358.44	1.19	108.43	–	–	–	–	–	–	–
helium	propane	10	3.35102	60.881	0.42	-0.04796	0.45	11.8959	5577.15	1.03	58.80	–	–	–	–	–	–	–
helium	1-propanol	6	2.57205	726.357	0.83	-0.01264	1.07	11.5368	6813.04	1.03	64.91	–	–	–	–	–	–	–
helium	2-propanol	6	3.15456	19.097	1.02	-0.01853	1.07	11.6037	6568.49	1.23	62.65	–	–	–	–	–	–	–
helium	propene	14	3.44370	-26.997	0.83	-0.04814	0.94	10.9143	1904.52	0.92	58.84	–	–	–	–	–	–	–
n-heptane	*n*-decane	5	5.83377	1629.896	1.41	0.00657	1.51	0.9631	132.45	1.65	6.81	–	–	34.06	22.77	18.52	30.40	28.81
n-heptane	*n*-dodecane	5	5.88128	1525.263	2.13	0.03617	2.04	0.8855	132.67	2.18	15.55	–	–	30.62	19.05	18.51	23.25	24.63
n-heptane	*n*-hexadecane	8	5.86950	1821.851	1.97	0.11016	2.80	0.7499	133.82	3.09	24.56	–	–	33.68	22.78	24.44	24.34	26.86
n-heptane	*n*-tetradecane	5	5.86900	1563.646	1.72	0.02093	1.81	0.8028	133.05	2.96	29.65	–	–	29.40	18.67	18.71	19.23	22.68
n-hexadecane	carbon dioxide	10	7.44580	2658.208	0.80	-0.16959	3.11	0.9379	278.97	1.91	34.82	–	–	12.21	33.40	102.80	61.01	24.25
n-hexadecane	carbon monoxide	10	7.38820	3229.109	3.02	-0.41183	3.27	1.0499	280.25	3.08	51.49	–	–	13.21	38.83	87.01	64.22	18.74
n-hexadecane	*n*-decane	5	7.47725	1688.803	1.09	-0.11191	11.12	0.4751	291.18	6.01	62.45	–	–	13.07	14.69	13.91	39.13	19.99
n-hexadecane	*n*-dodecane	5	7.42323	2187.317	1.95	-0.03193	4.88	0.3976	288.61	2.43	55.76	–	–	14.96	15.22	16.29	24.68	20.42
n-hexadecane	hydrogen	10	7.19512	5415.513	11.09	-1.15413	5.68	2.1314	268.40	7.32	37.24	–	–	55.28	70.82	23.96	83.58	38.35
n-hexadecane	*n*-octane	10	7.48244	1654.127	1.87	-0.09792	8.82	0.5159	289.46	3.65	64.04	–	–	13.88	18.00	16.54	42.79	19.16
n-hexadecane	*n*-tetradecane	5	7.42492	2085.948	1.79	-0.06702	7.32	0.3774	290.23	5.42	42.01	–	–	13.59	12.80	14.22	21.72	21.15
hexafluoroethane	helium	7	5.47382	-98.499	1.00	-0.06188	1.47	9.1955	658.59	1.69	83.63	–	–	–	–	–	–	–
n-hexane	acetone	5	5.37467	2344.055	2.19	-0.06288	2.31	1.4801	111.01	3.03	7.37	–	–	5.42	5.90	64.29	25.75	20.34

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-hexane	acetonitrile	7	5.58921	1344.997	3.13	-0.00058	5.82	1.1551	102.14	5.93	22.16	–	–	115.32	110.08	246.91	60.48	146.30
n-hexane	benzene	36	5.59189	1160.547	4.97	-0.02713	5.49	1.1371	103.51	14.54	26.17	–	–	80.10	82.83	114.18	74.29	88.03
n-hexane	carbon disulphide	10	5.58060	1120.254	1.92	0.04371	4.76	1.1409	102.23	4.66	64.04	–	–	178.18	168.35	362.18	98.69	224.06
n-hexane	naphthalene	20	5.55846	1343.473	4.65	0.04037	6.67	0.8828	98.35	15.15	10.14	–	–	49.57	45.58	44.12	49.47	46.00
n-hexane	phenanthrene	15	5.58888	1146.222	4.82	0.07799	6.54	0.6767	81.65	11.81	12.83	–	–	63.76	56.82	53.53	60.56	59.51
n-hexane	toluene	28	5.58119	1246.429	4.69	-0.01227	5.45	1.0354	102.80	16.17	18.14	–	–	78.86	82.91	106.45	76.21	85.17
n-hexane	1,3,5-trimethylbenzene	20	5.59790	1320.823	3.84	0.00347	5.22	0.8743	101.17	14.54	5.88	–	–	48.09	46.23	46.11	47.59	46.33
n-hexane	*m*-xylene	5	5.70366	565.161	2.23	0.00241	2.81	1.3601	115.15	2.00	5.49	–	–	6.24	11.30	36.87	6.26	11.14
n-hexane	*p*-xylene	17	5.64521	1017.461	5.51	0.02291	7.25	0.9088	93.68	16.35	8.34	–	–	56.45	54.15	49.43	56.94	54.22
krypton	argon	6	2.81603	806.166	0.96	-0.01771	1.96	5.6514	11563.83	2.91	32.57	–	–	–	–	–	–	–
krypton	helium	6	2.88873	248.576	0.78	-0.01227	1.45	22.0575	9617.38	2.38	81.76	–	–	–	–	–	–	–
krypton	neon	17	3.10569	464.846	1.21	-0.06838	1.95	9.0618	8120.62	2.92	53.32	–	–	–	–	–	–	–
krypton	xenon	8	2.94963	975.799	0.96	-0.02775	1.97	3.3325	13066.53	2.29	9.25	–	–	–	–	–	–	–
methane	carbon dioxide	10	3.76763	545.579	1.49	-0.00450	1.64	5.9479	6501.16	1.72	16.96	–	–	–	–	–	–	–
methane	tetrachloroethene	5	4.12257	892.336	0.11	-0.12146	0.57	2.8076	7640.69	0.11	110.69	–	–	–	–	–	–	–
neon	deuterium	5	2.27123	237.745	0.64	0.02278	2.46	24.0282	3212.22	1.12	46.96	–	–	–	–	–	–	–
neon	helium	24	2.34246	72.110	1.54	0.04915	1.64	28.0397	2125.92	1.25	57.07	–	–	–	–	–	–	–
neon	hydrogen	5	2.13472	-43.655	3.08	0.06364	2.00	31.7987	2881.11	0.63	61.10	–	–	–	–	–	–	–
neon	xenon	6	2.77048	185.938	0.73	-0.01774	0.75	6.4366	4241.29	0.78	61.51	–	–	–	–	–	–	–
nitrogen	acetone	5	3.48283	711.858	2.60	-0.04837	2.64	4.5745	12223.22	3.03	48.11	–	–	–	–	–	–	–

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
nitrogen	benzene	21	3.96017	297.248	2.93	-0.03707	3.04	2.8617	5026.96	2.99	64.24	–	–	–	–	–	–	–
nitrogen	carbon tetrachloride	5	4.03976	460.821	0.57	-0.06748	0.55	2.3629	4620.11	0.63	95.88	–	–	–	–	–	–	–
nitrogen	ethane	39	3.54484	545.442	1.67	-0.04035	1.94	5.0479	7764.35	1.80	16.66	–	–	–	–	–	–	–
nitrogen	helium	48	3.30563	69.042	2.79	0.02649	2.84	19.8919	3731.03	3.26	66.29	–	–	–	–	–	–	–
nitrogen	methane	25	3.44933	298.605	2.38	0.00814	2.38	7.3053	5634.88	2.30	19.20	–	–	–	–	–	–	–
nitrogen	propane	20	3.58932	604.241	2.25	-0.02432	2.49	3.9980	7627.80	2.28	41.10	–	–	–	–	–	–	–
nitrogen	trichloromethane	5	3.66845	605.926	1.14	-0.04440	1.19	3.0085	6469.87	1.21	69.50	–	–	–	–	–	–	–
octafluorocyclobutane	helium	7	7.01411	-196.972	0.05	-0.06066	0.82	7.5922	1758.11	0.15	86.39	–	–	–	–	–	–	–
octafluoropropane	helium	7	6.02359	1.163	0.62	-0.09218	0.85	7.9937	1817.27	0.15	85.90	–	–	–	–	–	–	–
n-octane	tetraethyltin	5	6.03957	2285.229	4.37	-0.00626	4.74	0.7116	148.73	6.31	17.69	–	–	20.42	26.20	53.34	13.76	24.33
oxygen	helium	8	3.03409	133.274	1.29	0.02530	1.41	21.0509	4501.28	1.36	66.70	–	–	–	–	–	–	–
oxygen	hydrogen	13	2.63782	120.472	0.82	0.04425	1.26	26.2335	6132.89	0.50	72.82	–	–	–	–	–	–	–
propane	helium	7	4.87232	-42.690	0.16	-0.03038	0.52	11.0417	2708.28	0.26	72.44	–	–	–	–	–	–	–
propane	1-octene	8	4.47172	947.408	1.64	0.08814	1.92	1.5602	57.26	1.91	9.91	–	–	7.32	27.75	34.70	19.51	26.64
propane	1-tetradecene	8	4.46040	738.243	1.69	0.13224	1.97	1.3094	58.74	1.92	40.78	–	–	16.66	25.61	15.79	24.66	19.75
propene	helium	7	4.62497	-32.952	0.06	-0.00422	0.38	12.2132	2875.60	0.13	72.48	–	–	–	–	–	–	–
sulfur hexafluoride	benzene	9	4.50844	1091.453	6.84	-0.03526	8.41	0.6679	1.44	10.58	7.33	16.16	–	39.39	51.09	42.39	39.89	47.80
sulfur hexafluoride	benzoic acid	6	4.38986	1771.403	1.52	-0.06603	4.99	0.6061	40.87	2.61	17.30	13.12	–	149.89	76.57	103.02	194.96	81.32
sulfur hexafluoride	carbon tetrachloride	6	4.80088	791.178	2.47	-0.00543	3.18	0.6877	35.40	5.18	13.73	21.28	–	37.99	33.97	31.82	42.27	32.10
sulfur hexafluoride	cyclohexane	5	4.84463	1006.778	0.13	-0.09743	0.92	1.1504	8141.63	0.12	2.50	–	–	–	–	–	–	–

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}··s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
sulfur hexafluoride	methylcyclohexane	5	3.98708	1627.358	0.25	-0.08403	1.73	1.1703	10547.92	0.32	11.66	–	–	–	–	–	–	–
sulfur hexafluoride	naphthalene	5	4.90149	-10.186	5.21	0.07964	5.47	1.1687	67.42	5.52	11.07	9.65	–	77.19	29.47	40.69	120.66	30.05
sulfur hexafluoride	toluene	11	3.84955	1950.339	6.00	-0.06356	11.39	0.5288	-18.56	9.73	7.21	12.93	–	37.76	51.56	44.06	35.72	49.77
sulfur hexafluoride	1,3,5-trimethylbenzene	10	3.88110	1950.487	4.04	-0.03742	10.37	0.5377	18.96	4.59	14.17	6.88	–	33.06	45.21	41.60	30.23	45.23
sulfur hexafluoride	*p*-xylene	52	4.62060	849.295	5.78	0.03271	7.57	0.5781	19.73	12.41	7.75	11.03	–	23.28	41.80	35.17	21.67	40.99
tetrafluoromethane	helium	7	4.31451	-11.057	0.05	0.01283	0.30	13.1087	3104.65	0.11	78.86	–	–	–	–	–	–	–
tetrafluoromethane	tetrachloroethene	5	4.98321	652.322	1.48	-0.04476	1.70	1.0459	3426.96	0.92	51.75	–	–	–	–	–	–	–
tetrafluoromethane	1,1,1-trichloroethane	5	4.42277	716.698	0.77	-0.00726	0.78	1.4470	7233.94	0.86	37.93	–	–	–	–	–	–	–
							Polar solvents											
acetone	benzene	6	4.64878	925.906	0.31	–	–	2.2845	63.64	0.34	–	–	–	13.32	6.14	18.91	6.90	0.42
acetone	biphenyl	6	4.66248	1122.885	0.41	–	–	1.6524	63.91	0.44	–	–	–	18.79	1.26	2.21	4.95	3.07
acetone	chlorobenzene	6	4.63780	1078.785	0.82	–	–	2.0016	63.38	0.88	–	–	–	13.57	3.53	15.35	2.56	1.00
acetone	ethylbenzene	6	4.64870	953.847	0.31	–	–	1.9295	63.58	0.36	–	–	–	19.02	6.48	5.23	3.61	5.30
acetone	naphthalene	5	4.66015	955.936	0.36	–	–	1.8206	63.71	0.45	–	–	–	18.33	4.04	4.86	0.43	3.93
acetone	*n*-propylbenzene	5	4.66072	905.110	0.64	–	–	1.8083	63.70	0.72	–	–	–	21.10	6.25	0.87	1.72	6.78
acetone	toluene	5	4.63548	1041.392	0.27	–	–	2.0722	63.50	0.35	–	–	–	16.89	6.81	10.51	5.62	3.54
acetone	1,2,4-trichlorobenzene	6	4.65153	1104.631	1.10	–	–	1.6838	63.45	1.26	–	–	–	11.48	3.21	14.26	6.99	3.84
acetone	1,3,5-trimethylbenzene	5	4.65525	963.390	0.32	–	–	1.7711	63.66	0.40	–	–	–	18.98	4.01	3.48	0.61	4.39
acetonitrile	carbon disulphide	5	3.97239	1396.373	1.98	–	–	2.1614	39.94	2.57	–	–	–	25.05	15.83	22.46	24.83	8.54
acetonitrile	methanol	20	3.96220	1788.894	1.63	–	–	2.2488	40.11	4.65	–	–	–	17.13	11.78	44.61	23.67	9.56

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
acetonitrile	[Bmim][bti]	5	4.21983	-785.027	0.34	–	–	2.2708	47.27	0.62	–	–	–	49.34	21.73	30.41	15.44	24.08
acetonitrile	[Emim][bti]	5	4.20061	-468.225	0.50	–	–	2.2007	46.88	0.84	–	–	–	46.88	19.68	27.09	14.33	21.88
acetonitrile	[Hmim][bti]	5	4.16806	-151.604	1.27	–	–	1.6746	45.70	1.55	–	–	–	48.77	19.34	29.49	11.85	21.87
acetonitrile	[Omim][bti]	5	4.14427	69.313	0.65	–	–	1.5377	45.45	0.80	–	–	–	49.17	18.58	29.82	10.10	21.18
n-butanol	ammonia	64	5.39793	1727.769	4.68	–	–	2.0578	89.73	8.67	–	–	–	210.78	157.43	495.01	83.79	287.72
n-butanol	carbon dioxide	66	5.23825	1447.505	3.86	–	–	2.3033	85.86	4.36	–	–	–	21.64	24.82	71.94	39.38	23.84
n-butanol	propane	98	5.28941	719.106	2.33	–	–	1.8294	87.62	3.73	–	–	–	30.08	29.65	64.22	26.17	37.29
n-butanol	propene	135	5.29645	434.271	3.38	–	–	2.1171	87.89	4.52	–	–	–	24.82	24.76	52.70	27.00	28.74
chlorobenzene	propene	32	5.39995	1971.673	1.29	–	–	1.6733	93.74	0.92	–	–	–	39.29	33.32	59.79	33.80	35.92
deuterium oxide	oxygen	18	3.11784	-2186.429	2.14	–	–	18.0990	17.85	2.28	–	–	–	18.03	16.26	31.58	8.49	12.00
ethanol	ammonia	18	4.38598	1025.485	4.00	–	–	3.0443	55.13	4.91	–	–	–	41.07	5.92	110.59	20.34	47.74
ethanol	benzene	21	4.33294	-204.157	4.11	–	–	2.6934	52.54	15.89	–	–	–	25.50	22.15	33.79	22.93	25.52
ethanol	benzonitrile	16	4.31158	793.057	1.70	–	–	2.0418	55.04	1.75	–	–	–	25.16	26.84	17.48	23.48	24.05
ethanol	benzyl acetate	15	4.27523	1513.234	1.96	–	–	1.4227	53.74	3.36	–	–	–	15.28	13.01	9.04	6.31	12.03
ethanol	1,2-butanediol	5	4.35681	1242.107	2.77	–	–	1.8458	55.93	7.82	–	–	–	28.70	22.53	44.50	26.15	29.45
ethanol	carbon dioxide	27	4.26113	379.865	4.32	–	–	4.4000	52.60	4.80	–	–	–	47.62	59.10	26.90	68.20	46.50
ethanol	dibenzyl ether	15	4.30543	930.410	2.31	–	–	1.4413	54.17	4.00	–	–	–	24.76	18.53	20.64	9.43	19.25
ethanol	ethylene glycol	5	4.35522	1567.226	2.47	–	–	1.8945	55.82	7.08	–	–	–	59.15	40.71	90.69	38.61	58.17
ethanol	glycerol	5	4.35596	1154.416	4.03	–	–	1.7485	56.11	10.35	–	–	–	52.51	42.70	73.54	45.40	52.69
ethanol	naphthalene	13	4.32870	-92.160	3.85	–	–	2.0019	48.80	8.18	–	–	–	15.35	16.36	22.21	22.15	17.93

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
ethanol	nitrous oxide	5	4.28901	-253.314	0.19	—	—	4.6893	53.24	0.16	—	—	—	44.94	56.73	23.86	66.23	43.93
ethanol	phenanthrene	13	3.39067	1749.448	3.27	—	—	1.2956	30.46	4.86	—	—	—	10.25	17.44	16.78	29.30	17.03
ethanol	2-phenylethyl acetate	15	4.28672	1490.055	1.86	—	—	1.3318	53.76	3.72	—	—	—	17.56	13.03	12.41	4.91	13.03
ethanol	3-phenylpropyl acetate	15	4.28828	1623.941	3.50	—	—	1.2311	53.92	5.18	—	—	—	13.65	7.27	8.74	3.16	7.84
ethanol	propane	30	4.33216	-134.493	2.93	—	—	3.5041	54.84	3.92	—	—	—	42.67	48.77	32.04	49.22	43.00
ethanol	propene	30	4.32340	-244.270	3.17	—	—	3.7826	54.60	4.22	—	—	—	45.33	52.12	33.86	53.10	45.67
ethanol	toluene	14	4.31620	-137.389	4.23	—	—	2.1947	46.76	8.99	—	—	—	19.00	15.88	29.73	19.22	19.93
ethanol	1,3,5-trimethylbenzene	13	4.32405	-17.152	4.06	—	—	1.9395	49.40	8.04	—	—	—	16.75	18.49	23.55	25.36	19.74
ethanol	water	15	4.43039	1210.854	3.73	—	—	3.1855	56.63	8.93	—	—	—	143.32	74.14	288.42	28.53	162.67
ethylene glycol	propene	31	4.58779	419.704	2.51	—	—	1.5060	55.16	2.57	—	—	—	48.85	50.92	30.46	48.70	44.24
methanol	acetonitrile	26	3.60293	2409.404	4.20	—	—	1.9707	30.41	8.70	—	—	—	26.98	38.70	18.86	37.89	29.55
methanol	ammonia	24	3.92593	989.981	4.65	—	—	4.8717	38.23	5.82	—	—	—	112.35	53.10	180.03	20.39	108.11
methanol	carbon dioxide	25	3.89285	-1320.984	2.85	—	—	9.4867	37.06	3.12	—	—	—	30.80	47.80	13.99	50.39	33.13
methanol	carbon monoxide	8	3.50807	2333.855	3.58	—	—	5.5379	34.92	3.79	—	—	—	15.85	36.13	10.06	39.34	18.05
methanol	*p*-chloronitrobenzene	18	3.91248	-902.158	0.63	—	—	3.8860	37.57	0.94	—	—	—	22.58	23.72	21.13	14.97	19.64
methanol	propane	27	3.80516	310.936	2.09	—	—	4.6752	36.39	2.55	—	—	—	25.81	35.95	19.39	34.02	27.95
methanol	water	5	4.65105	-1216.491	1.60	—	—	3.8954	37.55	1.72	—	—	—	292.95	171.71	450.29	108.40	292.99
methanol	[Bmim][bti]	11	3.88701	-493.678	3.19	—	—	2.6346	37.29	3.49	—	—	—	42.07	34.01	40.52	19.78	31.64
methanol	[Emim][bti]	11	3.90033	-756.284	2.71	—	—	2.9743	37.49	1.09	—	—	—	41.27	34.51	40.06	21.40	32.20
methanol	[Hmim][bti]	5	3.89388	-470.759	1.73	—	—	2.4797	37.54	1.49	—	—	—	38.05	28.06	35.96	11.55	25.40

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
methanol	[Omim][bti]	5	3.89234	-397.557	1.21	–	–	2.3105	37.45	1.30	–	–	–	39.02	27.96	36.51	10.51	25.18
methyl fluoride	helium	7	3.57802	-9.803	0.05	–	–	16.7414	3053.55	0.12	–	–	–	–	–	–	–	–
1-propanol	ammonia	31	4.78277	920.934	5.25	–	–	2.4773	72.62	8.35	–	–	–	45.10	14.63	146.82	16.65	66.13
1-propanol	carbon dioxide	27	4.67627	-3.307	2.66	–	–	3.7241	70.28	3.35	–	–	–	51.79	60.25	25.90	70.23	46.62
1-propanol	propane	36	4.72306	-650.453	2.99	–	–	2.5842	71.34	3.73	–	–	–	47.31	50.28	30.65	52.51	44.61
1-propanol	propene	36	4.71430	-684.688	2.60	–	–	2.8122	71.21	3.49	–	–	–	50.55	54.27	33.35	56.84	47.85
1-propanol	water	5	5.69086	-3367.301	2.16	–	–	1.7651	73.16	2.57	–	–	–	155.26	92.89	366.50	37.16	203.52
2-propanol	benzene	10	4.99431	-42.786	6.31	–	–	2.0985	68.23	10.91	–	–	–	10.57	13.02	34.02	12.26	16.45
2-propanol	*n*-decane	10	5.02141	196.055	4.13	–	–	1.5385	73.37	9.01	–	–	–	17.82	13.95	13.66	17.21	12.66
2-propanol	naphthalene	10	4.97765	349.843	6.41	–	–	1.5677	66.86	12.24	–	–	–	11.40	15.43	23.27	16.77	15.35
2-propanol	phenanthrene	9	5.02494	154.077	3.94	–	–	1.4024	70.77	8.89	–	–	–	11.59	18.24	18.91	22.44	16.63
2-propanol	*n*-tetradecane	9	4.98922	436.996	5.34	–	–	1.1721	70.60	10.34	–	–	–	15.19	17.36	12.97	27.18	14.06
2-propanol	toluene	10	4.98794	90.713	5.96	–	–	1.9048	68.14	10.62	–	–	–	10.78	13.30	26.93	13.21	15.05
2-propanol	water	5	5.10781	1978.189	2.01	–	–	1.7048	74.87	4.96	–	–	–	140.59	99.42	382.96	41.40	214.03
water	alanine	6	3.09298	-3045.874	0.57	–	–	21.7950	17.82	1.56	–	–	–	28.16	10.71	30.51	35.05	32.56
water	alloisoleucine	6	3.08859	-2838.074	0.40	–	–	18.2446	17.83	1.88	–	–	–	2.49	0.82	4.33	31.09	17.51
water	allothreonine	6	3.09070	-2811.028	0.47	–	–	19.3845	17.83	1.68	–	–	–	12.34	4.70	13.63	33.62	23.42
water	ammonia	5	3.13771	-4805.043	0.97	–	–	35.2132	17.78	2.43	–	–	–	36.59	2.95	55.11	7.58	31.15
water	arabinose	6	3.09110	-2575.645	0.92	–	–	18.7419	17.85	12.22	–	–	–	4.11	0.84	5.62	29.40	17.31
water	argon	8	3.12114	-3793.286	1.32	–	–	52.6166	17.92	6.47	–	–	–	50.62	9.05	70.13	19.71	44.70

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J\cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol\cdot cm^{-1}\cdot s^{-1}\cdot K^{-1/2}$)	V_D ($cm^3\cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	benzene	24	3.09520	-3705.863	2.26	—	—	25.5613	17.82	9.46	—	—	—	11.04	19.97	9.98	1.84	5.14
water	benzoic acid	12	3.09173	-3567.267	2.75	—	—	26.4755	17.86	2.70	—	—	—	15.72	20.45	14.67	2.88	6.33
water	biphenyl	7	3.08846	-3065.369	2.35	—	—	18.6941	17.82	8.84	—	—	—	19.93	19.05	17.59	8.41	4.75
water	*n*-butane	16	3.09744	-3227.560	8.62	—	—	32.4055	17.91	9.89	—	—	—	11.19	8.86	11.93	19.45	15.10
water	1,2-butanediol	5	3.09477	-3176.808	1.01	—	—	20.7916	17.82	11.45	—	—	—	2.19	6.80	2.87	17.91	10.07
water	1,3-butanediol	5	3.09392	-2987.751	0.36	—	—	19.1949	17.79	2.14	—	—	—	8.11	0.81	9.31	25.68	17.30
water	1,4-butanediol	5	3.09340	-3192.482	1.78	—	—	20.5989	17.82	10.83	—	—	—	2.28	6.84	2.97	18.10	9.98
water	*n*-butanol	13	3.09441	-3255.083	4.01	—	—	22.6052	17.83	9.31	—	—	—	3.81	7.93	4.40	15.78	8.98
water	2-methyl-1-butanol	6	3.09312	-3250.547	2.48	—	—	24.2610	17.87	12.05	—	—	—	6.51	12.39	5.40	12.18	4.42
water	3-methyl-1-butanol	6	3.09286	-3228.188	2.17	—	—	23.4173	17.86	12.61	—	—	—	4.72	10.72	3.59	14.32	5.19
water	2-methyl-2-butanol	6	3.09397	-3167.411	2.24	—	—	23.4421	17.87	12.76	—	—	—	4.13	8.13	4.17	17.64	8.24
water	3-methyl-2-butanol	6	3.09352	-3270.431	2.20	—	—	24.0493	17.87	12.62	—	—	—	5.32	11.28	4.53	13.60	5.30
water	*n*-butylbenzene	7	3.08933	-3180.148	3.32	—	—	18.6153	17.84	8.84	—	—	—	15.23	14.52	12.88	14.34	4.00
water	a-amino-n-butyric acid	6	3.09105	-2958.387	0.40	—	—	20.1748	17.83	1.74	—	—	—	9.32	1.31	10.54	28.86	19.50
water	caffeine	22	3.08745	-2742.764	0.84	—	—	17.1205	17.80	2.35	—	—	—	10.24	9.78	7.86	20.45	6.12
water	camphor	8	3.08707	-3075.731	0.74	—	—	23.8525	17.87	3.84	—	—	—	14.43	14.88	12.44	12.95	1.19
water	carbon dioxide	111	3.12007	-4639.758	3.62	—	—	48.2267	17.84	5.36	—	—	—	3.74	25.65	8.48	16.43	5.07
water	cinnamic acid	8	3.09015	-3855.775	2.10	—	—	34.5188	17.91	3.15	—	—	—	27.64	28.41	26.07	6.16	15.83
water	cyclohexane	10	3.09265	-3439.347	5.92	—	—	25.5002	17.87	10.39	—	—	—	7.11	12.94	6.74	11.86	6.77
water	cyclopentane	10	3.09440	-3253.074	3.21	—	—	26.8344	17.87	7.95	—	—	—	4.38	11.66	4.49	10.45	6.63

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J\cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol\cdot cm^{-1}\cdot s^{-1}\cdot K^{-1/2}$)	V_D ($cm^3\cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	diethylene glycol	5	3.08549	-2706.920	0.94	–	–	18.9049	17.78	0.80	–	–	–	2.86	4.68	3.73	21.46	12.41
water	*N*,*N*-diethylethanolamine	5	3.08993	-2661.661	0.10	–	–	15.3818	17.78	2.08	–	–	–	3.22	1.51	4.98	31.12	17.85
water	diglycolamine	5	3.08777	-2667.250	0.75	–	–	16.5597	17.76	0.68	–	–	–	7.44	1.87	8.73	29.25	18.79
water	dimethylethanolamine	5	3.08873	-2369.273	1.27	–	–	14.6623	17.74	3.18	–	–	–	18.36	9.25	19.68	38.64	28.94
water	dipropylene glycol	5	3.07833	-1911.200	0.58	–	–	13.7610	17.72	0.57	–	–	–	3.28	2.67	4.44	30.18	16.58
water	*meso*-erythritol	5	3.09338	-2770.697	1.25	–	–	17.9133	17.81	11.15	–	–	–	9.36	1.89	10.60	29.73	19.97
water	ethane	16	3.11345	-4205.256	3.46	–	–	34.7778	17.85	9.04	–	–	–	7.15	13.63	10.35	4.21	7.05
water	ethanol	22	3.10245	-3609.999	2.53	–	–	23.5426	17.75	4.57	–	–	–	10.84	7.98	14.15	10.24	12.01
water	ethylbenzene	16	3.09057	-3188.694	2.91	–	–	19.5821	17.82	10.85	–	–	–	9.52	13.20	8.18	12.72	3.23
water	ethylene glycol	9	3.10043	-3474.707	2.51	–	–	23.0235	17.78	1.81	–	–	–	13.69	3.10	16.17	17.38	16.59
water	1-ethylnaphthalene	7	3.08811	-3228.132	2.60	–	–	17.7474	17.83	9.10	–	–	–	16.37	15.01	13.82	14.23	2.35
water	galactose	6	3.08965	-2419.810	1.30	–	–	17.1534	17.85	12.76	–	–	–	1.18	0.98	2.63	32.31	17.26
water	glucose	10	3.08914	-2266.112	1.54	–	–	16.6379	17.84	8.22	–	–	–	10.02	7.44	12.03	41.01	26.31
water	glycerol	10	3.09081	-3454.173	1.40	–	–	21.2153	17.81	7.37	–	–	–	6.57	3.80	7.81	20.45	13.94
water	glycine	6	3.09121	-3535.915	0.44	–	–	24.1650	17.81	2.04	–	–	–	2.85	9.10	4.28	12.39	8.16
water	hexafluorobenzene	6	3.09409	-3304.907	0.88	–	–	18.7065	17.77	4.16	–	–	–	4.55	9.85	3.79	15.73	6.17
water	1,2,6-hexanetriol	5	3.08899	-2723.521	1.98	–	–	16.5032	17.80	2.32	–	–	–	1.66	2.90	3.34	30.14	16.54
water	homoserine	6	3.09023	-2884.832	0.61	–	–	19.8781	17.83	1.66	–	–	–	6.55	0.52	7.80	27.50	17.45
water	hydrogen	6	3.75205	-9961.208	0.78	–	–	137.2697	17.86	1.86	–	–	–	52.92	66.81	45.42	64.15	54.85
water	hydrogen sulfide	22	3.10708	-3780.667	2.97	–	–	28.1220	17.66	5.75	–	–	–	8.41	22.44	11.89	14.43	8.33

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	*myo*-inositol	5	3.08958	-2397.757	1.95	—	—	15.8241	17.83	10.32	—	—	—	8.28	5.65	10.24	38.59	24.20
water	isoleucine	6	3.08895	-2797.978	0.62	—	—	18.4523	17.84	1.63	—	—	—	2.12	1.07	3.98	30.75	17.17
water	krypton	6	3.11645	-3936.873	0.45	—	—	62.5603	17.90	1.90	—	—	—	6.33	20.31	16.58	10.71	2.78
water	lactose	5	3.07968	-2641.235	0.67	—	—	12.4908	17.80	1.62	—	—	—	1.73	7.59	6.67	48.09	27.16
water	leucine	6	3.08931	-2811.520	0.64	—	—	18.2549	17.84	1.69	—	—	—	2.83	1.25	4.70	31.66	17.98
water	*tert*-leucine	6	3.08922	-2879.592	0.50	—	—	18.5315	17.84	2.18	—	—	—	4.10	1.68	5.91	32.52	19.01
water	mannitol	5	3.08924	-2461.765	2.34	—	—	15.1837	17.82	10.76	—	—	—	5.35	4.19	7.62	37.78	22.49
water	mannose	6	3.08883	-2353.312	1.57	—	—	17.2846	17.85	12.23	—	—	—	1.81	2.00	1.99	30.31	15.49
water	methane	32	3.73999	-4052.542	4.51	—	—	39.8491	17.82	5.73	—	—	—	7.89	18.76	15.80	8.79	6.62
water	methanol	15	3.11470	-4463.864	4.61	—	—	33.9363	17.79	6.69	—	—	—	6.02	17.61	11.59	6.60	5.23
water	methyl bromide	6	3.10719	-4203.089	2.82	—	—	59.8353	17.93	1.90	—	—	—	5.26	17.14	6.65	4.32	5.40
water	methyl chloride	6	3.11237	-4665.551	2.45	—	—	65.0273	17.94	1.49	—	—	—	10.40	12.84	13.85	6.88	9.86
water	methylcyclopentane	10	3.09170	-3032.430	1.68	—	—	23.6457	17.86	10.50	—	—	—	4.36	10.77	3.48	13.96	5.18
water	methyl fluoride	6	3.12122	-5860.528	2.04	—	—	87.3643	17.95	2.14	—	—	—	8.93	23.78	9.83	12.87	9.47
water	*N*-methylpyrrolidone	5	3.09169	-3245.502	0.44	—	—	19.9466	17.78	2.13	—	—	—	4.59	11.12	3.49	13.39	4.78
water	monoethanolamine	5	3.09417	-3189.937	2.62	—	—	17.9064	17.64	4.50	—	—	—	6.69	13.88	6.49	6.45	6.07
water	monoisopropanolamine	5	3.09475	-2726.477	1.88	—	—	18.5617	17.80	0.73	—	—	—	12.21	3.11	13.46	28.66	20.86
water	naphthalene	7	3.09057	-3492.613	2.43	—	—	21.1846	17.82	8.80	—	—	—	20.42	22.32	18.97	2.15	8.68
water	2-naphthol	16	3.08935	-3693.647	3.92	—	—	24.4283	17.80	3.97	—	—	—	28.55	31.40	27.48	10.89	19.32
water	neon	6	3.13197	-5182.875	0.27	—	—	99.3936	17.84	1.81	—	—	—	21.76	48.89	4.93	47.24	24.19

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D (J·mol^{-1})	AARD	$k_{12,d}$	AARD	$B \times 10^7$ (mol·cm^{-1}·s^{-1}·K$^{-1/2}$)	V_D (cm^3·mol^{-1})	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	nitrous oxide	78	3.12074	-5260.695	8.32	–	–	51.5695	17.86	7.19	–	–	–	8.77	24.98	11.32	15.42	8.79
water	norleucine	6	3.08885	-2770.677	0.63	–	–	18.1508	17.83	1.57	–	–	–	1.97	1.00	3.88	31.09	17.29
water	norvaline	6	3.09042	-2850.271	0.63	–	–	19.2053	17.83	1.56	–	–	–	5.74	1.15	7.21	30.58	18.70
water	oxygen	34	3.12359	-4383.544	2.31	–	–	36.2355	17.75	5.76	–	–	–	18.28	14.66	34.05	6.85	13.60
water	pentaerythritol	6	3.08975	-2710.826	1.31	–	–	16.4411	17.80	10.25	–	–	–	2.71	1.32	4.28	28.62	16.25
water	*n*-pentane	8	3.09666	-3697.235	0.39	–	–	29.6614	17.90	12.01	–	–	–	8.36	12.50	7.90	11.19	6.92
water	2-methyl-2,4-pentanediol	5	3.09186	-2708.781	0.62	–	–	17.2307	17.81	1.94	–	–	–	1.98	1.44	3.69	29.26	16.28
water	1-pentanol	6	3.09291	-3321.936	2.84	–	–	24.3166	17.86	12.44	–	–	–	6.94	12.84	5.84	11.57	4.47
water	2-pentanol	6	3.09408	-3329.700	1.49	–	–	23.2386	17.86	13.64	–	–	–	5.36	11.30	4.63	13.57	4.50
water	3-pentanol	6	3.09388	-3237.624	2.05	–	–	23.8842	17.87	12.73	–	–	–	4.97	10.78	4.23	14.25	5.67
water	phenol	10	3.08381	-3315.899	13.21	–	–	7.6289	15.81	52.05	–	–	–	12.09	4.66	13.72	21.75	17.54
water	piperazine	5	3.08971	-2261.014	1.28	–	–	14.6156	17.73	3.03	–	–	–	13.89	5.73	15.18	34.63	24.70
water	2-piperidineethanol	5	3.08915	-2679.305	0.28	–	–	15.7182	17.78	1.56	–	–	–	3.33	1.10	5.27	32.83	18.85
water	propane	16	3.10506	-3816.996	5.00	–	–	34.5000	17.89	9.03	–	–	–	7.84	9.73	8.46	10.41	9.16
water	1-propanol	15	3.09950	-3433.597	3.06	–	–	23.5001	17.81	9.66	–	–	–	6.67	7.35	7.95	13.77	10.58
water	2,2-dimethyl-1-propanol	6	3.09375	-3243.373	1.65	–	–	23.5633	17.86	13.18	–	–	–	5.26	11.22	4.46	13.68	4.81
water	2-amino-2-methyl-1-propanol	5	3.09030	-2924.322	0.90	–	–	17.4820	17.77	1.30	–	–	–	6.91	1.39	8.13	26.94	17.34
water	2-propanol	12	3.09772	-3403.870	4.43	–	–	24.8727	17.83	9.52	–	–	–	7.63	7.46	8.99	14.29	11.49
water	2-methyl-2-propanol	9	3.09628	-3313.112	3.03	–	–	20.5461	17.82	11.38	–	–	–	7.12	5.17	8.26	22.39	15.13
water	propylene glycol	5	3.09206	-2826.847	0.82	–	–	22.2593	17.80	0.64	–	–	–	9.24	3.10	10.70	20.08	15.20

Table 1 (*Continued*)

System			New Model			TLSM$_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J\cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol\cdot cm^{-1}\cdot s^{-1}\cdot K^{-1/2}$)	V_D ($cm^3\cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	radon	6	3.10340	-3770.727	0.90	–	–	52.0612	17.92	1.94	–	–	–	14.03	7.89	19.06	7.95	13.32
water	salicylic acid	13	3.09159	-3549.648	2.27	–	–	27.1229	17.84	3.16	–	–	–	24.96	28.35	23.91	7.22	15.71
water	serine	6	3.09196	-2901.011	0.46	–	–	20.8117	17.82	1.53	–	–	–	13.69	2.92	15.00	29.09	21.84
water	sucrose	10	3.08222	-2219.011	2.34	–	–	13.1087	17.83	8.82	–	–	–	6.14	2.53	1.94	42.61	21.02
water	sulfolane	5	3.09156	-3478.668	0.42	–	–	19.9504	17.77	2.63	–	–	–	7.56	14.68	6.53	8.28	1.85
water	tetraethylene glycol	5	3.08316	-2174.445	0.64	–	–	13.5617	17.79	0.64	–	–	–	2.31	5.47	6.02	42.96	24.28
water	threonine	6	3.09162	-2750.655	0.41	–	–	19.4005	17.83	1.78	–	–	–	15.44	6.82	16.73	35.76	26.03
water	toluene	15	3.09391	-3416.502	1.85	–	–	22.1708	17.84	12.32	–	–	–	6.36	12.78	5.29	11.29	3.34
water	triethanolamine	5	3.08615	-2785.447	0.32	–	–	14.6247	17.77	1.51	–	–	–	0.52	0.50	2.90	33.51	18.00
water	triethylene glycol	5	3.08017	-1984.533	0.34	–	–	13.5011	17.74	0.53	–	–	–	5.38	4.14	7.62	37.64	22.42
water	valine	6	3.09057	-2870.656	0.45	–	–	19.4018	17.84	1.80	–	–	–	6.27	1.29	7.70	30.62	18.96
water	xenon	6	3.10745	-3964.130	0.68	–	–	53.5845	17.91	1.88	–	–	–	13.72	10.79	20.71	3.10	11.54
water	xylitol	5	3.08973	-2732.422	2.43	–	–	16.5785	17.81	10.60	–	–	–	2.21	1.94	3.65	29.30	16.28
water	xylose	6	3.09080	-2619.953	0.60	–	–	18.4174	17.85	12.82	–	–	–	2.85	0.91	4.49	29.46	16.78
water	[Bmim][BF_4]	11	3.08344	-3842.529	1.06	–	–	25.0194	17.81	3.67	–	–	–	49.02	46.05	46.53	25.72	36.23
water	[Bmim][bti]	18	3.08188	-3451.637	4.08	–	–	19.6922	17.81	6.39	–	–	–	50.31	43.47	45.52	18.73	32.25
water	[Bmim][CF_3SO_3]	5	3.06965	-2390.496	1.45	–	–	11.7382	17.58	1.87	–	–	–	38.09	32.90	34.22	7.79	20.39
water	[Bmim][Cl]	6	3.08328	-3876.819	1.67	–	–	26.6577	17.82	3.66	–	–	–	47.14	45.43	45.19	25.97	35.69
water	[Bmim][$MeSO_4$]	5	3.05178	-1693.992	1.01	–	–	11.3579	17.50	0.94	–	–	–	42.16	37.81	38.82	13.57	26.32
water	[Bmim][$OcSO_4$]	6	3.08345	-3830.973	3.54	–	–	21.5140	17.84	5.18	–	–	–	51.51	43.66	46.01	17.99	32.12

Table 1 (*Continued*)

System			New Model			$TLSM_d$		Dymond			Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Solvent (1)	Solute (2)	NDP	$\sigma_{LJ,1}$ (Å)	E_D ($J \cdot mol^{-1}$)	AARD	$k_{12,d}$	AARD	$B \times 10^7$ ($mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}$)	V_D ($cm^3 \cdot mol^{-1}$)	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	[Bmim][PF_6]	5	3.08270	-3979.564	1.31	–	–	23.0507	17.78	1.16	–	–	–	51.83	47.65	48.74	26.77	37.86
water	[Emim][BF_4]	5	3.07283	-3179.604	1.31	–	–	19.4488	17.66	1.10	–	–	–	46.75	45.51	44.98	26.46	35.83
water	[Emim][bti]	18	3.08230	-3479.102	3.53	–	–	21.2219	17.81	6.07	–	–	–	49.49	43.76	45.44	20.18	32.93
water	[Emim][$C_2H_5SO_4$]	11	3.08093	-3144.229	2.90	–	–	21.6441	17.80	4.08	–	–	–	42.67	39.25	39.83	16.30	28.19
water	[Emim][C_2N_3]	5	3.08298	-3884.406	0.36	–	–	22.0798	17.76	0.82	–	–	–	44.06	41.74	41.77	20.55	31.28
water	[Emim][CF_3SO_3]	5	3.08860	-3952.297	1.52	–	–	24.9967	17.83	2.00	–	–	–	43.45	40.45	40.83	18.26	29.67
water	[Emim][$MDEGSO_4$]	5	3.08321	-3500.648	2.43	–	–	19.2709	17.80	2.35	–	–	–	43.83	37.63	39.43	11.62	25.66
water	[Hmim][bti]	6	3.07858	-3196.949	1.63	–	–	17.8766	17.81	3.96	–	–	–	49.59	41.55	43.96	15.02	29.61
water	[Omim][bti]	6	3.07599	-2969.433	1.44	–	–	15.2296	17.77	4.55	–	–	–	49.86	40.85	43.49	13.10	28.42

Table 2. Calculated errors (AARD): global results per type of solvent, and grand averages.

Type of solvent	NS	NDP	New Model	TLSM$_d$	Dym	Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Non-polar and weakly polar	307	5958	2.65	3.87	5.09	38.19	8.95	26.26	16.53	19.09	21.93	70.61	26.63
Polar	180	2335	2.97	–	5.58	–	–	–	29.66	27.93	46.24	25.94	32.20
Total	487	8293	2.74	3.87	5.22	38.19	8.95	26.26	20.74	21.93	29.73	56.28	28.42

NS = number of systems; NDP = number of data points; AARD = average absolute relative deviation; Models: TLSMd = tracer Liu-Silva-Macedo; Dym = Dymond; Zhu = Zhu *et al.*; HYS = He-Yu-Su; LT = Lai-Tan; WC = Wilke-Chang; TC = Tyn-Calus; Scheib = Scheibel; RD = Reddy-Doraiswamy;LR = Lusis-Ratcliff

Table 3. Calculated errors (AARD): global results per physical state of the system, and grand averages.

Type of system	NS	NDP	New Model	TLSM$_d$	Dym	Zhu	HYS	LT	WC	TC	Scheib	RD	LR
Gaseous	73	1036	1.56	2.00	9.39	42.67	–	–	–	–	–	–	–
Supercritical	173	4398	2.90	4.14	4.04	37.25	8.95	26.26	13.59	15.87	16.86	73.34	24.45
Liquid	241	2859	2.92	5.18	5.53	37.28	–	–	31.79	31.25	49.52	30.03	34.52
Total	487	8293	2.74	3.87	5.22	38.19	8.95	26.26	20.74	21.93	29.73	56.28	28.42

Symbols: the same as in Table 2.

In Figures 1.a and 1.b the calculated diffusivities for both types of systems are plotted against their experimental values. These graphics show a good distribution along diagonal, which highlights model accuracy. It is also important to emphasize that the validation of the new model covered not only wide temperature and density ranges (from gas and liquid phases to supercritical fluids and compressed liquids close to the freezing line), but also systems composed of non-polar, weakly polar and polar molecules (solute and/or solvent), which can also be very distinct in terms of size and/or symmetry.

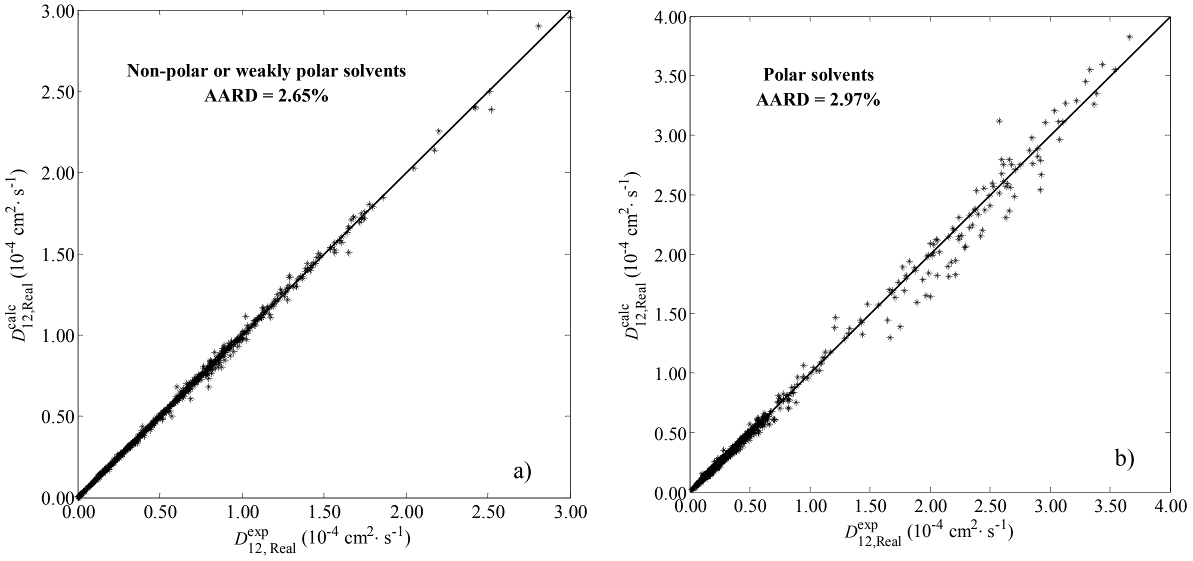

Figure 1. Comparison between calculated and experimental tracer diffusion coefficients for a) non-polar and weakly polar solvent systems and b) for polar solvent systems.

Since the LJ model cannot represent accurately the type and diversity of these molecules, one may expect that its parameters may take values without strict physical meaning when fitted to real data. In this work this happened only with activation energy, which took negative values in several systems (see Table 1). Nonetheless this is more desirable than increasing the complexity of the new model, by introducing for instance polar interactions and roughness parameters. Similar findings can be found in the literature, *e.g.* [20, 27]. Anyway, as has been mentioned above, excellent results were achieved for all real systems. Furthermore, it will be shown below that the new model exhibits fine predictive ability.

The global deviations achieved by the remaining models are also shown in Table 2. They vary from 3.87 % (in the case of $\mathrm{TLSM_d}$ model) to 70.61% (in the case of Reddy-Doraiswamy equation) for non-polar and weakly polar solvents systems, and 5.58% to 46.24% (in the case of Dymond and Scheibel correlations, respectively). It should be noted that $\mathrm{TLSM_d}$, Zhu *et al.*, and Lai-Tan equations are not appropriate for polar systems and accordingly they were not applied in this case. As may be observed, the deviations obtained by the majority of the models selected for comparison are very excessive in particular those of Zhu *et al.*, Lai-Tan, Wilke-Chang, Tyn-Calus, Scheibel, Reddy-Doraiswamy, and Lusis-Ratcliff. Nonetheless all individual results are listed in Table 1, since there are systems for which these models perform very well. In such cases readers may chose the simplest model for estimation. For instance, for divinylbenzene in carbon dioxide, 1-octene in ethane, and triethanolamine in water systems, the Wilke-Chang correlation gave rise to $\mathrm{AARD} =$ 3.74, 4.78, 0.52 %; for phenylacetic acid in carbon dioxide and phenanthrene in 2,3-dimethylbutane, the He-Yu-Su expression provided $\mathrm{AARD} =$ 1.62 and 2.49 %.

Concerning the free volume equation of Dymond, the two parameters embodied (B and V_D) can explain its enhanced results ($\mathrm{AARD} =$ 5.22%). Nonetheless, that performance is inferior to that achieved by our 2-parameter equation: 5.22% against 2.74%. Furthermore, the Dymond equation exhibits frequently physically meaningless results: quite different minimum diffusive free volumes (V_D) for the same solvent, which is not theoretically correct, and even negative values (see Table 1). For instance, for $\mathrm{CO_2}$ (solvent) the following V_D values were fitted: 1.19, -49.61, and 5898.70 $\mathrm{cm^3 \cdot mol^{-1}}$, for 15-crown-5, ethyl acetate, and hydrogen (solutes) respectively. Moreover, the Dymond equation should be used only for interpolation, which limits its application outside the fitting interval. On the other hand, the TLSM$_d$ model gave rise to particularly small deviations for non-polar and weakly polar solvent systems (only 3.87 %). However, it has been designed for non-polar or weakly polar systems only, and so it was not extended to the whole database compiled in this work.

In Figure 2 the optimized LJ diameters of all solvents, $\sigma_{1,\mathrm{LJ}}$, are plotted against their estimated values using Eqs. (15) and (16). It is evident their unbiased distribution along diagonal, though significant deviations to the bisector can be observed. This is a very important finding, if one attends to the work of Chen [65] about the rough hard sphere theory. He highlighted that the tracer diffusivities are rather insensitive to small variations in the solute diameter when the temperature is varied, while equivalent variations in the solvent diameter are considerably more important. Accordingly, in this work, the solute diameter was estimated by correlations given by Eqs. (15) or (16), whereas $\sigma_{1,\mathrm{LJ}}$ was taken as adjustable parameter. This approach contributed also to the good representations accomplished by our $D_{12,\mathrm{Real}}$ model.

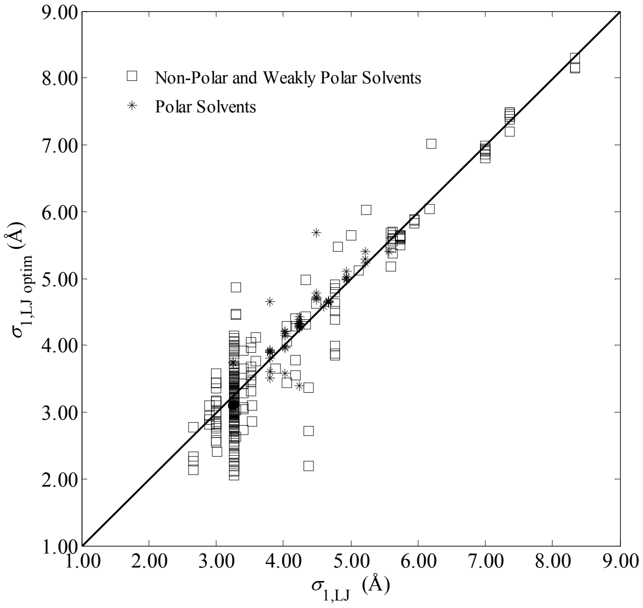

Figure 2. Optimized *versus* estimated Lennard-Jones diameter of the solvents of all systems studied in this work.

The prediction capability of the new model was also evaluated and compared with that of the Dymond correlation, since both embody two parameters: ($\sigma_{1,\mathrm{LJ}}$; E_D) and (B; V_D). For this purpose, 250 systems containing diffusivities at distinct temperatures were selected, (totalizing 4576 points), and both pairs of parameters were fitted to the highest temperature data. Subsequently, ($\sigma_{1,\mathrm{LJ}}$;E_D) and (B;V_D) were utilized to predict the diffusion coefficients for the remaining conditions. The average deviations obtained from the global fitting and prediction are listed in Table 4. The superiority of the prediction capability of our model is evident after comparing the AARDs found, *i.e.*, 3.46% (new model) *versus* 18.61% (Dymond). Besides, only small AARD increment was observed when passing from correlation to prediction with our model (3.01% → 3.46%), while Dymond equation behaved poorly in similar conditions (4.83% → 18.61%). This fact reinforces the reliability and theoretically sound basis of the new model. Actually, it can be recommended to estimate tracer diffusivities with good accuracy, when few data points can be measured or found in the literature for the preliminary optimization of the two parameters ($\sigma_{1,\mathrm{LJ}}$; E_D).

Table 4. Average absolute relative deviations computed for two situations: *i*) correlation of 250 systems using all 4576 points; and *ii*) prediction of the same diffusivities, using the parameters fitted to data at the highest temperatures.

Model	AARD (all data fitted)	AARD (prediction ability)
This work	3.01	3.46
Dymond	4.83	18.61

The behaviour of our model is further examined by graphing several tracer diffusivity isotherms of very distinct systems: *β*-carotene in carbon dioxide, dibenzyl ether in ethanol, and methanol in acetonitrile (Figures 3.a, 3.b and 3.c, respectively). Quite good representations are clearly accomplished in the three systems, being this performance similar for the remaining mixtures. In fact, such results are in accordance with the small AARDs obtained (2.74%, Table 2). It is worth noting the excellent results achieved for the aqueous systems whose solutes are ionic liquids: [Bmim][BF_4], [Bmim][bti], [Bmim][CF_3SO_3], [Bmim][Cl], [Bmim][$MeSO_4$], [Bmim][$OcSO_4$], [Bmim][PF_6], [Emim][BF_4], [Emim][bti], [Emim][$C_2H_5SO_4$], [Emim][C_2N_3],

[Emim][CF_3SO_3], [Emim][$MDEGSO_4$], [Hmim][bti], and [Omim][bti]. In all cases, the relative deviations were less than 4.08 %.

In Figures 4.a and 4.b a comparison is provided between the relative deviations of the diffusion coefficients calculated by the Dymond equation and by the new model. Figure 4.b points out an unbiased behaviour of the new model for almost all systems, whether constituted by non-polar, weakly polar or polar solvents, since they are very consistently scattered around zero. In contrast, the overestimation of Dymond correlation at high densities and its underestimation at low densities are clearly pointed out by Figure 4.a. Besides, the magnitude of the deviations computed by Dymond is exceptionally higher, mainly in the small diffusivity region (*i.e.*, almost 400%). These results evidence once again the good performance of the proposed model.

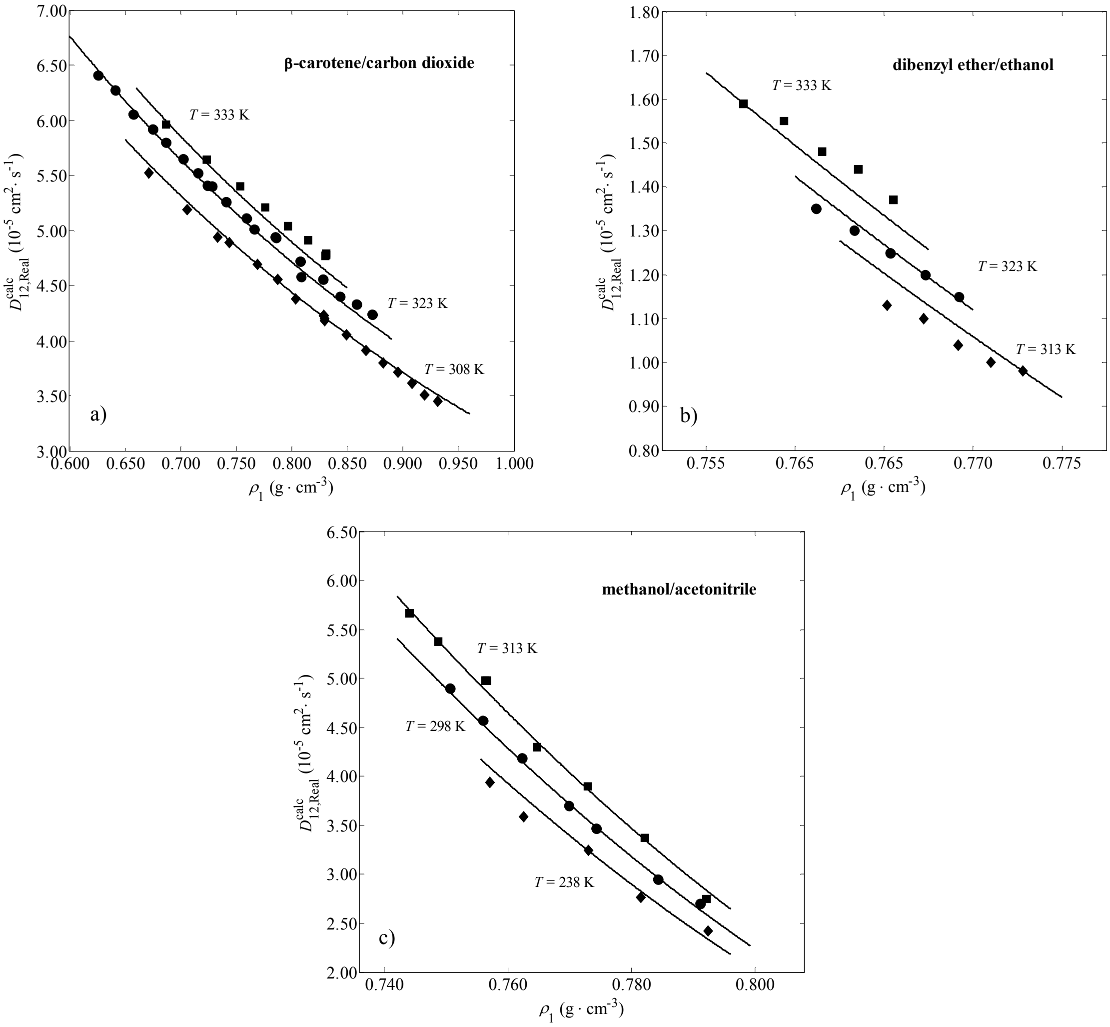

Figure 3. Tracer diffusion coefficients for the systems: a) *β*-carotene in carbon dioxide, b) dibenzyl ether in ethanol, and c) methanol in acetonitrile. Experimental data from references [66-70]; calculated results obtained by the new model.

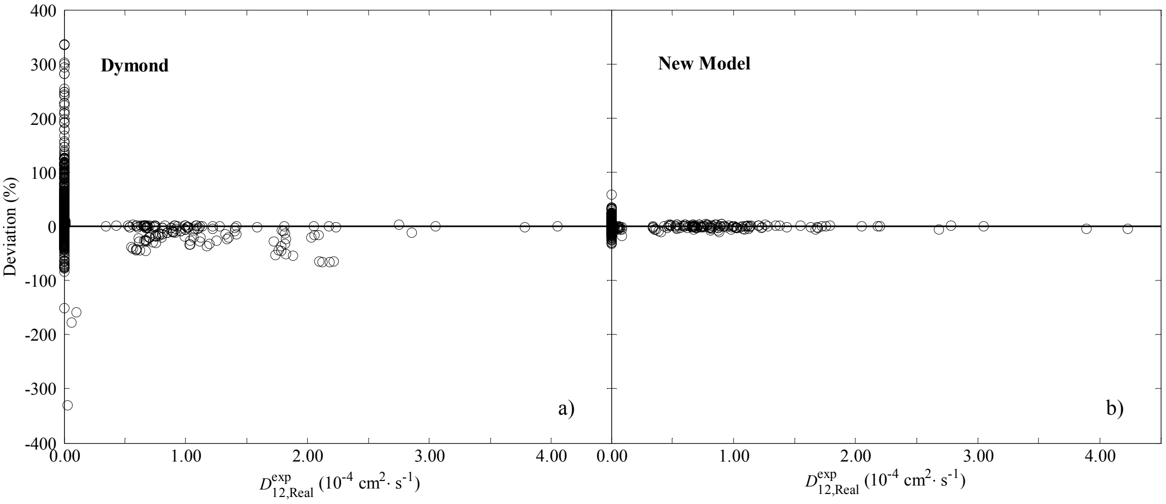

Figure 4. Relative deviations achieved by the a) Dymond equation, and by the b) new model as function of experimental diffusivities.

4.PVI.5. Conclusions

In this work a new model to estimate binary diffusivities at infinite dilution in gas, liquid and supercritical solvents is proposed and evaluated for polar and/or non-polar solute/solvent systems, which can also be very distinct in terms of size and symmetry. The model was validated with the largest database ever compiled, composed of 487 systems with 8293 data points, covering wide temperature and density ranges, giving rise to global average absolute relative deviation of only 2.74%, which highlights its fine accuracy and universal character. Besides, several models from the literature were selected for comparison, but almost all of them achieved deviations significantly higher, in particular the hydrodynamic correlations (20.74 – 56.28%). The expressions of Zhu *et al.* and He-Yu-Su are only applicable to non-polar/weakly polar solvents and supercritical systems, respectively, and attained 38.19% and 8.95%. The Dymond equation achieved 5.22% of error, but it should not be used for extrapolations. On the other hand, the new model offered excellent prediction capability, substantially superior to that of Dymond (AARD = 3.46% *versus* 18.61%, respectively), which reinforces its reliability and theoretically sound basis. A spreadsheet for D_{12} calculation is provided online for users in Supplementary Material.

Nomenclature

AARD	Average absolute relative deviation
B	Constant characteristic of the solvent-solute pair in Dymond equation
D_{12}	Tracer diffusion coefficient
$D_{12,\mathrm{LJ}}$	Tracer diffusion coefficient of LJ systems
$D_{12,\mathrm{Real}}$	Tracer diffusion coefficient of real systems (new model)
Dym	Dymond free-volume expression
E_D	Activation energy of the diffusion process
F_{12}	Correction factor of hard sphere system
$g(\sigma_{12})$	Radial distribution function at contact
HS	Hard-Sphere
HYS	He-Yu-Su correlation
k_B	Boltzmann constant
LJ	Lennard-Jones
LR	Lusis-Ratcliff equation
LT	Lai-Tan equation
M	Molecular weight
M_{12}	Reduced molar mass of the system
m	Mass of a molecule
m_{12}	Reduced mass of the system
N_a	Avogadro constant
N_1	Number of spheres
NDP	Number of data points
NS	Number of systems
P_c	Critical pressure
$\Re_\mathrm{g}$	Universal gas constant
RD	Reddy-Doraiswamy equation
Scheib	Scheibel equation
SCF	Supercritical fluid
T	Absolute temperature

T_c	Critical temperature
T_{bp}	Normal boiling point
TLSM$_d$	Tracer diffusion coefficient model due to Liu, Silva and Macedo
V	volume
V_c	Critical volume
V_D	Constant related primarily with the solvent in Dymond equation
V_{bp}	Molar volume at normal boiling point
WC	Wilke-Chang equation
Zhu	Model of Zhu *et al.*

Greek letters

α_{12}	Parameter
$\varepsilon_{i,\mathrm{LJ}}$	LJ parameter of component $i = 1,2$ or mixture $i = 12$
η_1	Solvent viscosity
$\varphi_{1,\mathrm{eff}}$	Effective HS packing fraction of the solvent
ρ_1	Solvent number density
$\rho_{r,1}$	Reduced density of the solvent using critical density
σ_i	Diameter of component $i = 1,2$ or mixture $i = 12$
$\sigma_{i,\mathrm{LJ}}$	LJ parameter of component $i = 1,2$ or mixture $i = 12$

Subscripts

1	Solvent
2	Solute
12	Binary
E	Enskog
eff	Effective hard sphere diameter
i	Molecule i
LJ	Lennard-Jones
Real	Real systems (new model)

Superscripts

0	Ideal gas
*	Reduced quantity

calc	Calculated by the new model
exp	Experimental

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Paper VII

Adapted from

Simple and Accurate Correlations for Diffusion Coefficients of Solutes in Liquids and Supercritical Fluids Over Wide Ranges of Temperature and Density

Journal of Supercritical Fluids, **2013**, 76, 94–114.

Abstract

The binary diffusion coefficients at infinite dilution, D_{12}, are fundamental properties in chemical engineering simulation and design. In this work, very simple and accurate expressions involving two parameters are proposed/analyzed for their estimation. They depend only on temperature and/or solvent density and/or solvent viscosity. Their correlation and prediction abilities are tested with the largest database ever compiled, composed of 539 binary systems and 8219 data points, where polar/non-polar, symmetrical/asymmetrical, small/large, and light/heavy molecules are included without exception. It is shown that only two experimental D_{12} values are sufficient to get good parameters for the subsequent estimation of reliable diffusivities far away from the conditions of the experimental data utilized to fit them. Globally, Eqs. (2) – (4) and (9) are recommended for D_{12} calculation, due to the excellent results achieved for both correlation (average errors between 2.78% and 3.05%) and prediction (average errors between 4.21% and 4.44%). A comparison with models from the literature is also accomplished.

4.PVII.1. Introduction

Reliable tracer diffusion coefficients, D_{12}, obtained experimentally, calculated via computer simulations or estimated by macroscopic models are fundamental in different engineering and industrial operations, to design and/or simulate processes involving mass transfer (*e.g.* multiphase chemical reactions, liquid-liquid and supercritical fluid extractions, distillation and absorption, adsorption and membranes, etc.) [1-5]. Their importance is not restricted to systems at infinite dilution, but also for subsequent prediction of the necessary coefficients for the concentrations found in real solutions [1, 6]. However, experimental diffusivities in the range of current applications of interest are not always available from literature, and accordingly accurate models are crucial to estimate them.

Transport properties are accurately represented at low densities by the kinetic theory, but up till now, it is not possible yet to give a rigorous interpretation of these properties in dense fluids. Several equations have been suggested in the literature to predict or correlate them by different approaches: free-volume theory [7-11], hydrodynamic theory [12-13], the Eyring activated-state theory [14], expressions based on idealized fluids [7, 15-23] (*e.g.* Hard Sphere, Square-Well, Lennard-Jones, and Repulsive Lennard-Jones), and the excess entropy scaling laws [7, 24-26]. Some of these models require a set of data for each pair of molecules in the mixture, such as critical properties, molecular weights, dipolar moments, Lennard-Jones force constants, molar volumes at normal boiling point, viscosity, etc. Some of these properties are not available being necessary to estimate them from proper correlations. Moreover, in many cases, the models available are specific for a particular physical state and, which is much more restrictive, are only applicable to either non-polar (at most weakly polar) or polar systems.

As a practical alternative, simple empirical and semi-empirical expressions obtained by correlation of experimental diffusivities could be utilized to interpolate missing data [27-28]. Temperature and pressure are operating conditions with direct strong impact upon D_{12}. Alternatively, one can attribute their influence via the solvent viscosity and density, as predicted by the hydrodynamic theory and free-volume models, respectively [7, 12-13]. Almost always temperature appears explicitly on D_{12} expressions.

At fixed pressure, the increment of system temperature enhances diffusion coefficient, as a consequence of molecular kinetic energy increase, which is more pronounced near the critical point of the solvent [15, 29], where compressibility is most significant. By increasing solvent density, the diffusion coefficient decreases as a result of the higher number of molecular collisions and the smaller mean free path between them [15, 30]. With respect to viscosity, which increases with increasing pressure but exhibits a much more complex dependence on the temperature, its role is frequently associated with a friction effect [3, 12]. Bearing in mind these two main trends, extremely simple two-parameter correlations are proposed in this work for the calculation of tracer diffusion coefficients of solutes in liquid and supercritical solvents. The correlations are very accurate, being applicable over wide ranges of temperature and density, for systems composed of polar and non-polar, symmetrical and asymmetrical, small and large, light and heavy molecules without exception.

4.PVII.2. Two-Parameters Correlations Under Investigation

The empirical and semi-empirical correlations presented in this work for the diffusion of a solute (2) through a solvent (1) were defined after evaluating the dependence of D_{12} $(\mathrm{cm^2 \cdot s^{-1}})$ on temperature, T (K), solvent viscosity, η_1 (cP), and solvent density, ρ_1 $(\mathrm{g \cdot cm^{-3}})$. Table 1 presents the set of nine expressions, (Eqs. (1) – (9)), investigated and validated in this work, some of which are proposed for the first time in the literature. They are divided into four different groups, taking into account the independent variables involved in the calculations. They are shown in linearized form, where a_i and b_i are the fitting parameters of equation i. The a_i coefficients are the slope of the correlations with respect to the main variable or group of variables (*i.e.*, T/η_1, $1/\eta_1$, $\ln\eta_1$, $\ln(T/\eta_1)$, ρ_1, $\ln\rho_1$) with the exception of Eq. (9), where both a_i and b_i are coefficients of independent

Table 1. Correlations analyzed in this work.

Independent variables	**Equation**	**Eq.**
T, η_1	$D_{12} = a_1 \dfrac{T}{\eta_1} + b_1$	(1)
	$\dfrac{D_{12}}{T} = a_2 \dfrac{1}{\eta_1} + b_2$	(2)
	$\ln\left(\dfrac{D_{12}}{T}\right) = a_3 \ln\eta_1 + b_3$	(3)
	$\ln(D_{12}) = a_4 \ln\left(\dfrac{T}{\eta_1}\right) + b_4$	(4)
η_1	$D_{12} = a_5 \dfrac{1}{\eta_1} + b_5$	(5)
	$\ln(D_{12}) = a_6 \ln\eta_1 + b_6$	(6)
T, ρ_1	$\dfrac{D_{12}}{T} = a_7 \rho_1 + b_7$	(7)
	$\dfrac{D_{12}}{T} = a_8 \ln\rho_1 + b_8$	(8)
T, ρ_1, η_1	$\dfrac{D_{12}}{T} = a_9 \rho_1 + \dfrac{b_9}{\eta_1}$	(9)

variables. All equations are explicit in the diffusivity, and possess only two specific parameters per system. In the following, a brief description is provided for each group.

4.PVII.2.1. Group 1 - Correlations based on the hydrodynamic theory

In the first group of equations, Eqs. (1) – (4), the diffusion coefficient is correlated with temperature and solvent viscosity. They consist of modifications of the Stokes-Einstein equation [2-3, 12]:

$$D_{12} = \frac{k_{\mathrm{B}}\, T}{6\, \pi\, \eta_1\, r_2} \tag{10}$$

where k_{B} is the Boltzmann's constant, and r_2 is the radius of the solute molecule. Stokes-Einstein model was firstly derived assuming that a large rigid spherical molecule of solute is moving through a continuum of solvent ($r_1 << r_2$) under infinitely dilute conditions [3, 12], where the system is considered an ideal mixture. Several well-known models in the literature follow this dependence ($D_{12} \propto T/\eta_1$) as, for instance, Wilke-Chang [12-13, 31] and Tyn-Calus [12, 32] equations. Those models were originally developed for liquid systems, being commonly extended with relative success to supercritical fluids [11, 13, 20-22, 33]. Nonetheless, this approach has been shown to fail in the supercritical region at lower densities given the significant amount of clustering around the solutes, which results in an overestimation of the diffusion coefficients [13].

Equation (1) is the common representation of D_{12} against temperature and solvent viscosity usually adopted in order to check if a system obeys or not the hydrodynamic behaviour. Eq. (2) is a modification of the previous one, whereby D_{12} possesses a temperature dependent intercept. Both Eqs. (1) and (2) fail the theoretical Stokes-Einstein limit of zero diffusivity when solvent viscosity tends to infinite. However, small deviations to the null intercept have been seen to persist for supercritical systems [27].

In Eq. (3), parameter a_3 must be negative but may be different from -1, while maintaining the null intercept and the temperature dependence of Stokes-Einstein (see Eq. (10)); if additionally $a_3 = -1$, that seminal model is recovered. This correlation has been used successfully by Funazukuri *et al.* [34] for supercritical and liquid states, but they have considered that for a specific molecule, both self- and binary diffusions are well represented by the same equation, *i.e.* the fitted parameters are only solute-dependent. On the other hand, parameter a_4 in Eq. (4) is positive and may be different from unit, giving rise to the nonlinear dependence of D_{12} upon T/η_1. When $a_4 = 1$, the Stokes-Einstein equation is once again obtained.

4.PVII.2.2. Group 2 - Correlations depending explicitly only on solvent viscosity

Equations (5) and (6) of Table 1 are the simplest expressions tested in this work. The tendencies of these correlations were observed by Suárez *et al.* [27] only for a few supercritical systems. The main differences between them are: *i*) The dependence on solvent viscosity, η_1^{-1} in Eq. (5) and $\eta_1^{a_6}$ in Eq. (6); *ii*) Eq. (6) satisfies the vanishing limit of Stokes-Einstein, while Eq. (5) deviates by the small intercept b_5.

4.PVII.2.3. Group 3 - Correlations depending explicitly on solvent density and temperature

The couple of Eqs. (7) and (8) adopt the density as the main solvent property. It is worth noting that Eq. (7) is very similar to the model proposed by Grushka *et al.* [35] based on the free-volume theory:

$$\frac{D_{12}}{T} = C\,(\rho_{\mathrm{D}} - \rho_1) \tag{11}$$

where C is a constant characteristic of the binary system, and ρ_{D} is a limiting density for which the binary diffusivity vanishes. The model of Grushka *et al.* [35] can be obtained from Eq. (7) after substituting $a_7 = -C$ and $b_7 = C\,\rho_{\mathrm{D}}$. Eq. (8) is a new correlation devised for supercritical mixtures or systems where the density variation range is high.

4.PVII.2.4. Group 4 - Correlation depending explicitly on solvent density and viscosity, and temperature

Equation (9) is the last expression considered in this work. It combines simultaneously the influence of the density and solvent viscosity on D_{12}/T, and may be observed as an additive combination of Eqs. (2) and (7).

4.PVII.3. Models Adopted for Comparison

In this paper three tracer diffusivity models were adopted for comparison: the 2-parameter correlation of Dymond [7, 36-37], the 1-parameter tracer-Liu-Silva-Macedo (TLSM$_d$) model [7, 20, 38], and the predictive hydrodynamic expression of Wilke-Chang [12-13, 31]. In the following, these expressions are summarily presented.

4.PVII.3.1. ***Dymond free-volume model*** [7, 36-37]

This model embodies two adjustable parameters: B is a constant characteristic of the solvent-solute pair, and V_D is a constant related primarily with the solvent. The binary diffusivity is expressed as function of the solvent molar volume, V_1:

$$D_{12} = B\sqrt{T}\left(V_1 - V_D\right) \tag{12}$$

4.PVII.3.2. ***Wilke-Chang equation*** [12-13, 31]

$$D_{12}\left(\mathrm{cm^2\,s^{-1}}\right) = 7.4\times10^{-8}\,\frac{T\sqrt{\phi_1\,M_1}}{\eta_1\,V_{\mathrm{bp},2}^{0.6}} \tag{13}$$

where ϕ_1 is a dimensionless association factor of the solvent, η_1 is the solvent viscosity (cP), M_1 is the solvent molecular weight $(\mathrm{g\cdot mol^{-1}})$, and $V_{\mathrm{bp},2}$ is the solute molar volume at its normal boiling point $(\mathrm{cm^3\cdot mol^{-1}})$.

4.PVII.3.3. ***TLSM$_d$ model*** [7, 20, 38]

The tracer diffusion coefficient model derived by Liu, Silva and Macedo [7, 20, 38], TLSM$_d$, corresponds to the following set of equations:

$$D_{12}\left(\mathrm{cm^2\,s^{-1}}\right) = \frac{21.16}{\rho_1\sigma_{12,\mathrm{eff}}^2}\left(\frac{1000\,\Re_{\mathrm{g}}T}{M_{12}}\right)^{\frac{1}{2}}\exp\left(-\frac{0.75\rho_{1,\mathrm{eff}}^*}{1.2588-\rho_{1,\mathrm{eff}}^*}-\frac{0.27862}{T_{12}^*}\right) \tag{14}$$

where $\Re_{\mathrm{g}} = 8.3144$ $(\mathrm{J\cdot mol^{-1}\cdot K^{-1}})$ is the universal gas constant, ρ_1 $(\mathrm{cm^{-3}})$ is solvent number density. The reduced number density of solvent ($\rho_{1,\mathrm{eff}}^*$), reduced temperature

(T_{12}^{*}), and reduced molar mass of the system (M_{12}, $\mathrm{g\cdot mol^{-1}}$) are calculated by:

$$\rho_{1,\mathrm{eff}}^{*} = \rho_1 \, \sigma_{1,\mathrm{eff}}^{3} \tag{15}$$

$$T_{12}^{*} = \frac{T}{\varepsilon_{\mathrm{LJ},12}/k_{\mathrm{B}}} \tag{16}$$

$$M_{12} = \frac{M_1 M_2}{M_1 + M_2} \tag{17}$$

where $\sigma_{\mathrm{LJ},12}$ and $\varepsilon_{\mathrm{LJ},12}$ are the binary LJ parameters (diameter and energy) computed from the single ones by the following combining rules:

$$\frac{\varepsilon_{\mathrm{LJ},12}}{k_{\mathrm{B}}} = \frac{8\sqrt{\sigma_{\mathrm{LJ},1}^{3}\,(\varepsilon_{\mathrm{LJ},1}/k_{\mathrm{B}})\times\sigma_{\mathrm{LJ},2}^{3}\,(\varepsilon_{\mathrm{LJ},2}/k_{\mathrm{B}})}}{(\sigma_{\mathrm{LJ},1}+\sigma_{\mathrm{LJ},2})^{3}} \tag{18}$$

$$\sigma_{\mathrm{LJ},12} = \left(1 - k_{12,\mathrm{d}}\right)\frac{\sigma_{\mathrm{LJ},1}+\sigma_{\mathrm{LJ},2}}{2} \tag{19}$$

and $k_{12,\,\mathrm{d}}$ is an adjustable parameter. The effective binary and single diameters, $\sigma_{12,\mathrm{eff}}$ and $\sigma_{1,\mathrm{eff}}$, take into account the influence of temperature upon the size of the molecules. An equation of the Boltzmann type has been adopted for their calculation [7, 16-17, 20, 38]:

$$\sigma_{n,\mathrm{eff}} = \sigma_{\mathrm{LJ},n}\,2^{1/6}\left[1+\sqrt{1.3229\,T_n^{*}}\right]^{-1/6} \tag{20}$$

where $n=1$ or 12, and $T_n^{*} = T/(\varepsilon_{\mathrm{LJ},n}/k_{\mathrm{B}})$. The LJ force constants of any component i may be taken from the original article [16] or, for substances not covered in that essay, are calculated by the corresponding states correlations (with critical constants in K and bar) published by Silva *et al.* [7, 17]:

$$\frac{\varepsilon_{\mathrm{LJ},i}}{k_{\mathrm{B}}} = 0.774\,T_{\mathrm{c},i}\,,\; i=1,2 \tag{21}$$

$$\begin{aligned}&\sigma^3_{\mathrm{LJ},i}(\text{Å}^3)=0.17791+11.779\left(\frac{T_{\mathrm{c},i}}{P_{\mathrm{c},i}}\right)-0.049029\left(\frac{T_{\mathrm{c},i}}{P_{\mathrm{c},i}}\right)^2,\ \text{if}\ T_{\mathrm{c},i}/P_{\mathrm{c},i}\le 100\\&\sigma_{\mathrm{LJ},i}(\text{Å})=0.809\ V_{\mathrm{c},i}^{1/3},\ \text{if}\ T_{\mathrm{c},i}/P_{\mathrm{c},i}>100\end{aligned}\qquad(22)$$

4.PVII.4. Database and Data for the Calculations used in Models Validation

In this work the largest database of tracer diffusivities in liquid and supercritical solvents was compiled for the calculations: 539 binary systems containing 8219 data points. In Table S1 (Supplementary Data), detailed information about database is given: systems studied, ranges of reduced temperature, pressure and solvent density (reduction performed with the critical constants), number of data points (NDP), and data sources. As much as possible, all data published were applied, but graphical information was rejected. Table S2 in Supplementary Data contains the name, molecular formula, CAS number, molecular weight, critical constants (T_{c}, P_{c} and V_{c}), molar volume at normal boiling point and Lennard-Jones force constants of all molecules involved in the calculations. All data sources are identified.

The solvent densities and viscosities reported together with the diffusivity data were always used. In contrast, when these properties were omitted they were taken from NIST database or calculated by a set of correlations: Yaws [39], Cibulka and Zikova [40], Cibulka *et al.* [41-42], and Cibulka and Takagi [43]. In the case of carbon dioxide the density and viscosity were estimated by Pitzer and Schreiber [44] and Altunin and Sakhabetdinov [45], respectively; for water they were calculated by IAPWS-IF97 [46]. The unknown critical constants were estimated by Joback [12, 47-48], Ambrose [12, 49-50], Klincewicz [12, 51], Somayajulu [52], Wen-Qiang [53], Constantinou-Gani [54] methods. For ionic liquids, the critical constants were taken from Valderrama and Rojas [55]. The molar volumes at normal boiling point were estimated by Tyn Calus [12, 56] equation.

4.PVII.5. Results and Discussion

In Table 2, the average absolute relative deviations (AARD) obtained with the correlations proposed in Table 1 (Eqs. (1) – (9)) and the three models adopted for comparison are shown for the binary systems studied. All detailed results may be found in Table S3 of Supplementary Data: systems, fitting parameters, 95% confidence intervals, coefficients of determination (R^2), and AARDs. The numerical solution was performed in Matlab 2009a® using the *regress* function in most of the cases. The individual results achieved with Dymond, TLSM$_d$, and Wilke-Chang models are also included in Table S3 (Supplementary Data). The percent deviations were calculated by:

$$\mathrm{AARD}\,(\%) = \frac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \frac{\left| D_{12,i}^{\mathrm{calc}} - D_{12,i}^{\mathrm{exp}} \right|}{D_{12,i}^{\mathrm{exp}}} \tag{23}$$

Table 2 shows that the relative deviations are generally very good, mainly for Eqs. (1) – (4), (6) and (9), for which they lie between 0.03 and 13.3%. On the other hand, Eqs. (5), (7) and (8) exhibit higher errors (41.09% for benzene in *n*-hexane, 32.12% for toluene in *n*-hexane, and 29.78% for phenol in water, respectively). The fitted parameters shown in Table S3 (Supplementary Data) embody in most cases expected physical meanings. For instance, the a_i are positive in Eqs. (1), (2), (4) and (5), which ensures the correct trends of D_{12} with temperature and viscosity ($\partial D_{12}/\partial T > 0$ and $\partial D_{12}/\partial \eta_1 < 0$), and are negative in Eqs. (3), (6) – (8), in order to guarantee that $\partial D_{12}/\partial \eta_1 < 0$ and $\partial D_{12}/\partial \rho_1 < 0$. Regarding parameters b_i, their signals are not so obviously fixed as those of a_i, which is mathematically simple to grasp after inspecting the various correlations. Nonetheless it is worth noting three consistent observations: b_7 and b_9 are always positive, whereas for Eq. (8) they are positive for all systems involving carbon dioxide and water as solvents.

Table 2. Calculated results (AARD) for the correlations under analysis (Eqs. (1) – (9)) and the three models adopted for comparison.

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
acetone	benzene	6	0.36	0.36	0.37	0.37	1.16	0.46	0.38	0.34	0.36	0.34	–	13.32
acetone	biphenyl	6	0.39	0.39	0.42	0.42	1.01	0.42	0.39	0.52	0.41	0.44	–	18.79
acetone	chlorobenzene	6	0.85	0.81	0.73	0.73	0.81	0.68	0.74	0.95	0.76	0.88	–	13.57
acetone	ethylbenzene	6	0.39	0.39	0.41	0.41	1.19	0.55	0.43	0.35	0.39	0.36	–	19.02
acetone	naphthalene	5	0.42	0.42	0.44	0.44	1.03	0.53	0.45	0.51	0.44	0.45	–	18.33
acetone	*n*-propylbenzene	5	0.76	0.76	0.76	0.76	1.30	0.87	0.79	0.67	0.75	0.72	–	21.10
acetone	toluene	5	0.38	0.39	0.40	0.41	1.25	0.52	0.42	0.33	0.38	0.35	–	16.89
acetone	1,2,4-trichlorobenzene	6	1.22	1.19	1.14	1.14	0.88	0.99	1.15	1.33	1.15	1.26	–	11.48
acetone	1,3,5-trimethylbenzene	5	0.43	0.43	0.44	0.44	1.28	0.55	0.47	0.35	0.43	0.40	–	18.98
acetone	water	4	0.85	0.90	0.97	0.98	1.01	1.00	0.92	0.88	0.89	0.87	–	85.11
acetonitrile	carbon disulphide	5	6.35	6.35	7.35	7.35	6.35	7.35	3.98	3.29	6.52	2.57	–	25.05
acetonitrile	methanol	20	1.65	1.58	1.52	1.57	3.35	3.36	3.53	3.26	1.60	4.65	–	17.13
acetonitrile	[Bmim][bti][a]	5	1.05	1.13	1.40	1.40	0.54	1.42	0.58	0.74	1.06	0.62	–	49.34
acetonitrile	[Emim][bti][b]	5	1.26	1.31	1.47	1.47	0.74	1.49	0.77	0.95	1.24	0.84	–	46.88
acetonitrile	[Hmim][bti][c]	5	1.94	1.91	1.86	1.86	1.49	1.88	1.46	1.61	1.86	1.55	–	48.77
acetonitrile	[Omim][bti][d]	5	0.85	0.84	0.85	0.85	0.78	0.85	0.81	0.80	0.88	0.80	–	49.17
1-butanol	ammonia	64	5.73	5.57	5.07	5.07	4.96	4.87	7.99	7.80	5.06	8.67	–	38.33
1-butanol	carbon dioxide	66	6.10	5.58	3.85	3.80	5.39	3.74	4.04	4.19	5.97	4.36	–	46.02
1-butanol	propane	98	2.93	2.95	2.92	2.84	2.70	2.70	3.27	3.24	3.10	3.73	–	49.58
1-butanol	propene	135	4.31	4.36	4.48	4.44	4.23	4.38	4.34	4.20	4.53	4.52	–	49.18

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	acetone	214	3.63	3.65	3.56	3.50	3.67	3.43	5.09	3.70	3.61	5.11	4.28	5.64
carbon dioxide	acridine	6	2.59	2.07	2.02	2.48	3.57	3.52	1.81	1.97	2.24	2.85	1.95	4.93
carbon dioxide	adamantanone	8	2.49	2.49	2.37	2.37	2.49	2.37	2.21	2.40	2.55	2.59	2.54	18.17
carbon dioxide	allylbenzene	15	2.65	2.14	1.91	2.36	3.80	3.63	1.68	2.12	2.22	3.34	2.99	5.36
carbon dioxide	aniline	15	1.64	1.66	1.38	1.34	2.14	1.89	1.49	1.93	1.64	2.46	2.98	33.34
carbon dioxide	anisole	15	2.43	2.26	1.70	1.81	2.77	2.40	1.39	1.97	1.92	2.97	2.06	7.33
carbon dioxide	anthracene	22	2.89	2.84	1.89	1.87	4.09	3.00	7.90	3.39	1.92	1.75	3.88	10.38
carbon dioxide	arachidonic acid (AA)	75	1.78	1.35	1.19	1.56	3.62	3.50	1.35	1.21	1.40	2.51	2.13	9.70
carbon dioxide	AA ethyl ester	48	0.95	0.94	0.86	0.86	3.00	2.98	2.63	1.29	0.83	1.17	2.43	15.16
carbon dioxide	behenic acid ethyl ester	17	0.74	0.76	0.73	0.72	1.44	1.42	1.72	0.93	0.77	0.86	3.66	21.34
carbon dioxide	benzene	249	6.78	6.72	6.75	6.79	6.97	6.99	6.63	6.68	6.84	7.49	7.38	8.76
carbon dioxide	benzoic acid	35	5.98	5.80	5.83	5.99	7.38	7.43	6.20	5.89	5.75	6.36	5.50	10.18
carbon dioxide	benzyl acetate	15	2.26	2.25	2.26	2.28	3.02	2.99	1.81	1.93	2.30	3.02	2.21	7.79
carbon dioxide	benzylacetone	15	2.65	2.30	1.87	2.22	3.61	3.38	1.78	2.55	2.08	3.76	2.32	6.19
carbon dioxide	biphenyl	24	3.01	2.91	2.89	2.95	3.56	3.51	2.94	2.79	2.91	3.39	3.41	10.13
carbon dioxide	2-bromoanisole	15	2.79	2.53	2.28	2.51	3.64	3.46	1.75	2.31	2.42	3.66	2.37	16.52
carbon dioxide	bromobenzene	21	4.22	4.25	4.03	4.00	4.32	4.09	3.74	4.13	4.31	4.45	4.48	6.32
carbon dioxide	2-butanone	40	2.01	1.85	1.61	1.78	3.15	2.85	1.67	1.59	1.72	2.59	1.91	5.13
carbon dioxide	*N*-(4-methoxybenzylidene)-4-*n*-butylaniline	5	0.31	0.31	0.32	0.32	0.31	0.32	0.26	0.28	0.31	0.33	1.77	17.85
carbon dioxide	*n*-butylbenzene	15	1.87	1.66	1.41	1.55	2.96	2.84	0.99	1.62	1.58	2.97	1.90	6.29

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*tert*-butylbenzene	15	2.80	2.75	2.63	2.68	3.64	3.61	1.87	2.42	2.74	3.62	3.87	7.92
carbon dioxide	butyric acid ethyl ester	16	1.49	1.52	1.51	1.46	2.38	2.39	1.93	1.56	1.51	1.89	3.64	4.31
carbon dioxide	caffeine	25	5.95	5.49	4.92	5.33	7.43	6.72	4.79	5.06	5.09	6.62	7.92	19.34
carbon dioxide	capric acid ethyl ester	16	1.44	1.47	1.34	1.32	2.06	1.89	2.20	1.60	1.40	1.44	3.85	13.46
carbon dioxide	caprylic acid ethyl ester	16	1.40	1.42	1.43	1.42	2.22	2.19	1.81	1.38	1.43	1.67	2.93	10.23
carbon dioxide	β-carotene	90	1.82	1.52	1.44	1.75	3.05	2.99	1.40	1.36	1.51	2.26	1.38	14.88
carbon dioxide	L-carvone	27	2.94	3.13	3.11	2.91	1.97	1.97	3.29	3.20	3.15	2.62	3.51	3.66
carbon dioxide	chlorobenzene	21	3.07	3.03	2.81	2.82	3.42	3.20	2.54	2.91	3.10	3.37	3.24	5.80
carbon dioxide	chrysene	4	1.93	1.73	1.72	1.95	4.16	4.16	1.43	1.43	1.75	2.61	1.45	16.16
carbon dioxide	citral	15	2.74	2.69	2.46	2.46	3.84	3.70	2.39	2.31	2.47	4.31	3.19	8.63
carbon dioxide	cobalt(III) acetylacetonate	38	1.46	1.36	1.27	1.36	3.35	3.14	1.63	1.27	1.41	2.13	1.59	11.53
carbon dioxide	copper(II) trifluoroacetylacetonate	12	4.70	4.66	4.73	4.78	5.12	5.17	4.26	4.53	4.82	5.04	4.73	37.09
carbon dioxide	15-crown-5	29	4.33	4.35	3.10	3.09	4.27	3.04	2.05	3.67	4.00	5.98	5.18	7.85
carbon dioxide	dibenzo-24-crown-8	28	1.68	1.62	1.55	1.60	2.06	1.99	1.32	1.51	1.62	1.93	2.06	12.73
carbon dioxide	cycloheptanone	8	1.70	1.70	1.67	1.67	1.70	1.67	1.87	1.65	1.64	1.85	2.95	24.01
carbon dioxide	cyclononanone	8	2.45	2.45	2.45	2.45	2.45	2.45	2.84	2.56	2.45	2.33	3.25	17.62
carbon dioxide	cyclopentanone	8	0.95	0.95	0.94	0.94	0.95	0.94	1.13	0.95	0.95	1.03	1.04	20.31
carbon dioxide	*n*-decane	5	1.37	1.45	1.39	1.31	1.68	1.58	1.62	1.49	1.50	1.47	3.70	38.51
carbon dioxide	dibenzyl ether	15	2.17	1.87	1.79	2.08	3.37	3.22	1.32	1.88	1.96	3.22	2.14	5.32
carbon dioxide	1,2-dichlorobenzene	15	1.74	1.39	1.53	1.85	3.00	3.02	2.09	1.49	1.40	2.07	1.48	6.89

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	1,3-dichlorobenzene	4	1.03	1.03	1.12	1.12	1.03	1.12	0.77	0.94	1.03	1.11	3.78	11.52
carbon dioxide	*p*-dichlorobenzene	13	3.47	3.43	3.35	3.37	3.80	3.73	3.48	3.30	3.53	3.72	3.54	10.61
carbon dioxide	diethyl ether	17	6.34	6.30	5.58	5.44	5.90	5.10	9.58	5.00	5.20	5.53	16.19	10.54
carbon dioxide	1,2-diethylbenzene	15	1.71	1.41	1.30	1.54	2.83	2.74	1.12	1.52	1.45	2.61	1.79	6.19
carbon dioxide	1,4-diethylbenzene	15	2.63	2.54	2.19	2.20	3.40	3.09	1.86	2.74	2.24	4.06	2.98	5.65
carbon dioxide	diisopropyl ether	15	6.39	6.09	5.59	5.61	6.34	5.95	9.27	4.84	5.56	7.87	12.60	7.14
carbon dioxide	2,3-dimethylaniline	15	1.95	2.02	1.75	1.64	2.15	2.02	1.62	1.91	1.92	2.38	1.95	16.04
carbon dioxide	2,6-dimethylaniline	15	2.88	2.48	2.01	2.41	3.79	3.55	1.57	2.18	2.49	3.34	2.66	11.47
carbon dioxide	1,1'-dimethylferrocene	68	2.08	2.08	1.60	1.69	2.68	2.60	2.52	1.55	2.05	3.67	2.78	12.16
carbon dioxide	2,6-dimethylnaphthalene	6	4.10	4.10	3.86	3.86	4.10	3.86	3.62	3.94	4.02	4.24	3.84	7.15
carbon dioxide	2,7-dimethylnaphthalene	6	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.50	4.51	4.50	4.35	6.91
carbon dioxide	2,4-dimethylphenol	15	3.22	2.67	2.27	2.70	4.12	3.79	1.97	2.42	2.57	3.63	2.58	9.42
carbon dioxide	diolein	9	1.36	1.36	1.14	1.14	1.36	1.14	0.80	1.13	1.47	1.61	1.64	23.69
carbon dioxide	1,3-divinylbenzene	15	1.37	1.31	1.46	1.55	2.09	2.19	1.56	0.90	1.34	1.39	1.09	3.74
carbon dioxide	docosahexaenoic acid (DHA)	63	0.99	0.95	0.69	0.76	2.62	2.59	0.72	0.82	0.97	1.63	1.38	7.28
carbon dioxide	DHA ethyl ester	65	0.81	0.84	0.84	0.82	2.51	2.51	2.19	1.20	0.83	1.45	2.28	16.73
carbon dioxide	DHA methyl ester	17	0.64	0.65	0.65	0.64	1.27	1.27	1.37	0.73	0.65	0.92	2.99	16.76
carbon dioxide	*n*-dodecane	5	2.84	2.98	2.87	2.73	3.23	3.07	3.20	3.03	3.09	2.99	5.39	40.87
carbon dioxide	eicosapentaenoic acid (EPA)	55	0.91	0.69	0.62	0.84	3.05	2.99	1.26	0.76	0.74	1.79	1.20	7.79
carbon dioxide	EPA ethyl ester	48	1.09	1.08	0.92	0.93	2.93	2.88	2.87	1.50	0.94	1.06	2.80	14.98

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	EPA methyl ester	17	0.63	0.61	0.56	0.58	1.10	1.07	1.68	0.85	0.62	0.49	3.62	17.37
carbon dioxide	ethanol	24	2.88	2.88	2.51	2.51	2.88	2.51	2.15	2.61	2.78	3.21	3.00	11.29
carbon dioxide	ethyl acetate	16	6.36	6.93	7.10	6.64	5.46	5.78	8.64	6.85	6.65	7.47	19.00	17.59
carbon dioxide	ethylbenzene	15	1.68	1.65	1.37	1.36	2.32	2.20	1.26	1.44	1.53	2.28	2.07	7.44
carbon dioxide	ethyl benzoate	15	3.16	3.14	3.14	3.18	3.17	3.12	2.99	2.79	3.17	2.94	4.93	3.88
carbon dioxide	2-ethyltoluene	15	3.14	2.96	2.59	2.77	4.07	3.77	2.17	2.75	2.93	3.76	3.28	8.95
carbon dioxide	3-ethyltoluene	15	3.21	2.99	2.61	2.79	4.12	3.82	2.55	3.15	2.94	4.00	3.59	11.68
carbon dioxide	4-ethyltoluene	15	1.74	1.51	1.18	1.39	2.83	2.65	2.14	2.25	1.44	3.07	2.68	7.46
carbon dioxide	eugenol	15	2.50	2.44	2.48	2.46	2.89	2.78	2.02	2.43	2.54	3.58	3.36	17.29
carbon dioxide	ferrocene	107	2.80	2.68	2.19	2.37	3.74	3.54	4.32	2.05	2.68	6.96	4.35	17.43
carbon dioxide	2-fluoroanisole	15	1.77	1.36	1.32	1.62	2.92	2.79	1.12	1.35	1.42	2.58	1.66	18.48
carbon dioxide	fluorobenzene	15	2.99	2.75	2.44	2.59	3.68	3.50	3.06	3.38	2.56	4.22	3.64	11.04
carbon dioxide	3-fluorophenol	4	0.93	0.93	1.02	1.02	0.93	1.02	0.67	0.84	0.92	1.00	3.86	13.15
carbon dioxide	geraniol	4	0.33	0.33	0.38	0.38	0.33	0.38	0.29	0.30	0.31	0.38	3.91	3.34
carbon dioxide	*n*-heptane	5	1.00	1.03	0.92	0.88	1.21	1.11	1.27	1.09	1.05	1.00	3.31	28.91
carbon dioxide	2-heptanone	11	2.03	2.03	1.89	1.89	2.03	1.89	2.66	2.22	2.09	1.83	4.47	30.11
carbon dioxide	4-heptanone	9	0.54	0.54	0.52	0.52	0.54	0.52	0.95	0.63	0.55	0.47	2.19	36.53
carbon dioxide	hexachlorobenzene	14	2.53	2.31	1.30	1.56	2.83	2.38	0.80	2.01	2.70	4.18	7.77	10.99
carbon dioxide	1-hexadecene	11	10.22	9.84	8.75	9.18	11.71	10.98	8.18	9.50	9.23	11.75	11.13	16.17
carbon dioxide	1,1,1,5,5,5-hexafluoroacetylacetone	15	4.02	4.01	3.87	3.84	3.97	3.79	3.30	3.76	4.18	4.36	4.08	18.95

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*n*-hexane	5	2.09	2.11	2.01	1.98	2.29	2.12	2.35	2.18	2.13	2.09	2.85	22.91
carbon dioxide	iodobenzene	20	2.44	2.25	1.93	2.02	2.86	2.60	1.79	2.09	2.23	2.82	2.62	9.02
carbon dioxide	D-limonene	15	3.09	2.92	3.00	3.09	4.17	4.10	3.49	2.76	2.95	4.06	3.15	9.32
carbon dioxide	linalool	15	2.82	2.79	2.64	2.64	2.99	2.93	2.34	2.68	2.75	4.02	3.49	7.24
carbon dioxide	linoleic acid	71	2.91	2.35	1.83	2.32	4.77	4.31	1.33	1.99	2.34	3.73	3.25	9.63
carbon dioxide	linoleic acid methyl ester	21	1.56	1.49	1.48	1.57	2.43	2.42	1.49	1.47	1.48	1.66	1.40	15.74
carbon dioxide	α-linolenic acid	56	2.01	1.53	1.44	1.89	4.28	4.21	1.66	1.30	1.57	2.79	1.83	14.24
carbon dioxide	γ-linolenic acid	142	1.57	1.17	1.13	1.52	3.89	3.84	1.55	1.11	1.24	2.15	2.79	7.79
carbon dioxide	γ-linolenic acid ethyl ester	41	5.85	5.45	5.53	5.73	8.07	8.11	5.89	4.62	5.38	5.10	6.27	6.92
carbon dioxide	γ-linolenic acid methyl ester	52	4.34	4.54	4.34	4.42	6.01	6.04	5.08	3.88	4.32	7.58	5.39	13.41
carbon dioxide	L-menthone	23	3.20	3.34	3.36	3.19	2.06	2.05	3.61	3.46	3.35	2.81	4.05	5.18
carbon dioxide	methanol	10	1.78	1.78	1.49	1.49	1.78	1.49	1.11	1.57	2.08	2.14	3.90	16.79
carbon dioxide	2-methylanisole	15	2.27	2.09	1.57	1.70	2.87	2.69	1.19	1.83	1.91	2.79	1.99	9.67
carbon dioxide	4-methylanisole	15	2.57	2.42	1.85	1.88	2.92	2.49	1.27	2.11	2.03	3.21	2.41	17.52
carbon dioxide	1-methylnaphthalene	11	5.49	4.66	3.89	4.77	7.23	6.75	3.52	4.31	4.76	6.64	10.02	20.35
carbon dioxide	methyl orange	60	4.04	4.10	4.17	4.13	4.43	4.45	4.68	4.22	4.07	4.13	–	–
carbon dioxide	monoolein	11	1.00	1.00	0.79	0.79	1.00	0.79	0.47	0.80	1.04	1.22	1.40	8.71
carbon dioxide	myristic acid ethyl ester	16	1.67	1.71	1.69	1.65	2.26	2.27	1.38	1.52	1.63	2.14	3.84	15.97
carbon dioxide	myristoleic acid	42	2.14	1.50	1.39	1.95	4.35	4.28	1.37	1.30	1.68	2.66	4.06	5.68
carbon dioxide	myristoleic acid methyl ester	81	10.74	10.61	10.34	10.20	13.89	13.63	10.30	8.55	10.35	10.33	9.86	10.43

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	naphthalene	114	7.51	7.69	7.55	7.38	6.97	6.75	10.61	7.51	7.84	9.76	9.98	10.84
carbon dioxide	1-naphthol	11	0.43	0.43	0.39	0.39	0.94	0.95	2.02	0.79	0.41	0.88	2.18	5.77
carbon dioxide	2-naphthol	16	3.01	2.86	1.86	1.89	3.04	2.04	6.37	2.69	2.28	1.73	2.53	7.84
carbon dioxide	2-nitroanisole	15	1.77	1.47	1.08	1.45	2.95	2.81	0.89	1.15	1.50	2.39	1.63	11.47
carbon dioxide	nitrobenzene	23	2.47	2.36	1.76	1.90	2.93	2.49	1.45	2.09	1.95	2.90	1.92	8.19
carbon dioxide	3-nitrotoluene	15	3.28	3.01	2.38	2.57	3.77	3.40	1.93	2.69	2.58	3.96	2.74	4.00
carbon dioxide	*n*-nonane	5	1.43	1.46	1.33	1.27	1.65	1.52	1.72	1.53	1.49	1.43	3.65	36.45
carbon dioxide	2-nonanone	10	2.33	2.33	2.35	2.35	2.33	2.35	2.30	2.32	2.34	2.35	4.21	35.76
carbon dioxide	5-nonanone	12	1.36	1.36	1.16	1.16	1.36	1.16	1.99	1.54	1.38	1.10	4.95	34.31
carbon dioxide	*n*-octane	5	1.66	1.69	1.54	1.50	1.88	1.70	1.95	1.76	1.72	1.66	3.65	33.41
carbon dioxide	oleic acid	19	1.57	1.57	1.02	1.02	1.57	1.02	0.52	1.12	1.68	2.14	2.52	10.03
carbon dioxide	oleic acid ethyl ester	5	2.33	2.33	2.65	2.65	2.33	2.65	3.40	2.23	1.91	0.97	5.87	5.72
carbon dioxide	oleic acid methyl ester	21	2.84	2.84	2.94	2.94	2.84	2.95	4.57	2.61	2.92	3.73	9.49	7.29
carbon dioxide	palladium(II) acetylacetonate	125	3.49	3.04	2.76	3.23	6.32	6.04	2.42	2.47	2.92	4.65	2.86	21.93
carbon dioxide	palmitic acid ethyl ester	17	0.58	0.57	0.57	0.58	1.07	1.05	1.48	0.79	0.60	0.61	3.18	15.14
carbon dioxide	*n*-pentane	5	1.67	1.70	1.58	1.55	1.88	1.69	1.93	1.76	1.72	1.67	3.15	13.23
carbon dioxide	2-pentanone	23	2.06	2.00	1.64	1.70	2.27	1.91	1.37	1.67	1.91	2.52	2.06	4.45
carbon dioxide	3-pentanone	46	2.16	2.01	1.96	2.11	3.15	3.06	2.28	1.88	2.05	2.62	2.17	8.28
carbon dioxide	2,4-dimethyl-3-pentanone	8	2.45	2.45	2.45	2.45	2.45	2.45	2.84	2.56	2.45	2.33	3.25	11.25
carbon dioxide	2,2,4,4-tetramethyl-3-pentanone	9	0.76	0.76	0.76	0.76	0.76	0.76	1.08	0.84	0.76	0.76	2.92	27.01

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*n*-pentylbenzene	31	2.38	2.30	1.99	2.30	6.13	6.07	1.56	1.81	2.03	3.86	2.04	8.38
carbon dioxide	phenanthrene	25	4.27	3.98	4.04	4.37	5.35	5.40	4.25	3.93	3.98	4.39	4.88	15.48
carbon dioxide	phenol	109	3.37	3.04	2.58	2.90	4.22	3.86	2.71	2.73	2.85	4.66	3.12	21.20
carbon dioxide	phenylacetic acid	16	1.49	1.47	1.45	1.47	2.16	2.14	1.70	1.39	1.48	1.80	2.01	4.25
carbon dioxide	phenylacetylene	15	0.96	0.88	1.03	1.12	2.10	2.20	1.17	0.79	0.88	1.58	1.22	7.80
carbon dioxide	1-phenyldodecane	15	2.39	2.19	2.14	2.28	3.16	3.03	1.58	2.01	2.20	3.14	2.37	6.96
carbon dioxide	1-phenylethanol	15	2.17	1.93	1.76	1.95	3.11	2.94	1.14	1.80	1.89	3.15	1.84	10.31
carbon dioxide	2-phenylethanol	15	2.11	1.77	1.67	1.97	3.36	3.23	1.11	1.65	1.87	3.03	2.00	12.10
carbon dioxide	2-phenylethyl acetate	15	2.19	1.87	1.79	2.04	3.37	3.22	1.41	1.71	1.96	3.06	2.09	8.63
carbon dioxide	1-Pphenylhexane	15	1.97	1.75	1.68	1.84	2.85	2.72	1.27	1.72	1.75	2.71	1.95	7.52
carbon dioxide	phenylmethanol	15	1.61	1.52	1.48	1.56	2.38	2.40	1.14	1.45	1.57	2.54	1.79	13.91
carbon dioxide	1-phenyloctane	15	2.42	2.14	1.93	2.19	3.68	3.56	1.73	2.28	2.08	3.65	2.57	8.65
carbon dioxide	3-phenylpropyl acetate	15	2.72	2.23	2.17	2.63	3.93	3.78	1.84	2.15	2.29	3.37	2.56	7.12
carbon dioxide	α-pinene	15	3.21	3.22	3.13	3.13	4.24	4.19	4.50	3.27	3.15	3.83	3.61	7.00
carbon dioxide	β-pinene	15	3.64	3.44	3.05	3.16	4.72	4.40	2.29	3.10	3.23	4.97	3.59	11.72
carbon dioxide	2-phenyl-1-propanol	15	1.54	1.42	1.35	1.51	2.56	2.49	0.88	1.38	1.49	2.64	1.73	9.72
carbon dioxide	3-phenyl-1-propanol	15	1.54	1.56	1.61	1.58	2.09	2.09	1.45	1.44	1.57	2.28	2.17	6.21
carbon dioxide	1-propanol	17	2.95	2.95	2.85	2.85	2.95	2.85	2.81	2.91	2.91	3.00	4.99	15.43
carbon dioxide	2-propanol	18	1.99	1.99	1.77	1.77	1.99	1.77	1.47	1.84	2.15	2.21	3.97	9.57
carbon dioxide	*i*-propylbenzene	36	2.14	2.19	2.18	2.13	2.68	2.66	2.89	2.19	2.19	2.32	2.22	8.75

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	*n*-propylbenzene	60	3.28	3.18	2.49	2.69	3.88	3.47	2.62	2.80	3.28	4.54	8.21	11.89
carbon dioxide	pyrene	21	3.46	3.43	2.80	2.79	4.03	3.48	7.32	4.00	2.86	2.92	4.78	9.75
carbon dioxide	squalene	5	1.80	1.80	1.92	1.92	1.80	1.92	1.57	1.72	1.75	1.87	4.89	13.56
carbon dioxide	stearic acid	4	0.53	0.53	0.52	0.52	0.53	0.52	0.58	0.55	0.53	0.52	1.34	50.32
carbon dioxide	stearic acid ethyl ester	17	0.70	0.70	0.69	0.68	1.48	1.47	1.38	0.80	0.70	1.03	3.45	16.25
carbon dioxide	styrene	15	2.93	2.97	2.95	2.90	2.92	2.81	3.38	3.76	3.06	4.39	4.10	5.38
carbon dioxide	*n*-tetradecane	5	2.91	3.21	3.16	2.86	3.56	3.48	3.31	3.23	3.27	3.32	7.77	38.78
carbon dioxide	tetrahydrofuran	15	6.18	6.23	5.91	5.76	5.69	5.12	10.09	4.93	5.32	4.99	14.70	15.96
carbon dioxide	thenoyltrifluoroacetone	15	3.12	3.29	3.29	3.12	2.69	2.66	3.68	3.23	3.42	3.05	3.09	30.20
carbon dioxide	α-tocopherol	82	1.63	1.34	1.28	1.57	3.05	2.93	1.38	1.17	1.37	2.21	1.32	31.55
carbon dioxide	toluene	35	3.59	3.97	3.47	3.17	2.93	2.57	3.37	3.67	3.82	4.14	4.29	5.32
carbon dioxide	triarachidonin	27	0.59	0.59	0.49	0.49	0.59	0.49	0.78	0.47	0.69	0.82	3.16	17.49
carbon dioxide	trierucin	101	2.74	2.19	1.88	2.47	3.59	3.34	1.60	1.91	2.47	2.95	4.99	13.57
carbon dioxide	trifluoroacetylacetone	15	1.88	1.78	1.75	1.84	2.64	2.61	1.83	1.61	1.79	2.18	1.82	3.74
carbon dioxide	1,3,5-trimethylbenzene	34	3.69	3.58	3.38	3.59	4.43	4.21	3.01	3.34	3.88	4.01	4.31	6.27
carbon dioxide	trinervonin	38	2.60	2.06	1.80	2.45	3.59	3.39	1.57	1.79	2.34	2.86	4.11	16.62
carbon dioxide	triolein	14	1.90	1.76	1.23	1.25	2.21	1.53	1.75	1.35	2.04	2.91	3.36	29.49
carbon dioxide	ubiquinone CoQ10	80	3.48	3.10	2.98	3.35	5.24	5.08	2.70	2.84	3.08	4.09	2.69	13.90
carbon dioxide	*n*-undecane	5	1.73	1.83	1.73	1.63	2.07	1.92	2.02	1.87	1.90	1.85	4.47	40.94
carbon dioxide	6-undecanone	13	2.76	2.76	2.53	2.53	2.76	2.53	3.41	2.96	2.69	2.53	4.89	36.53

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
carbon dioxide	vanillin	15	1.96	1.91	2.02	2.08	2.60	2.65	2.49	2.05	1.89	2.03	1.92	12.64
carbon dioxide	vitamin K$_1$	17	2.23	2.23	2.08	2.08	2.23	2.08	1.69	2.02	2.30	2.43	2.36	27.24
carbon dioxide	vitamin K$_3$	22	2.42	2.42	2.27	2.27	2.42	2.27	2.92	2.28	2.57	2.92	3.82	9.59
carbon dioxide	xater	24	3.00	3.46	3.10	2.40	5.01	4.59	4.24	3.79	3.49	4.18	13.05	56.20
carbon dioxide	*m*-xylene	12	7.45	7.66	8.03	8.15	10.93	10.94	10.88	6.39	7.81	10.53	20.09	17.73
carbon dioxide	5-*tert*-butyl-*m*-xylene	31	1.86	1.88	1.59	1.72	5.10	5.07	1.29	1.72	1.66	3.10	2.26	8.49
carbon dioxide	*p*-xylene	7	3.56	3.52	3.59	3.64	3.85	3.88	3.79	3.59	3.48	3.54	3.48	6.55
chlorobenzene	propene	32	1.08	1.02	0.87	0.84	0.64	0.70	1.01	1.06	0.95	0.92	–	9.75
chlorotrifluoromethane	acetone	10	5.37	5.37	4.80	4.80	5.37	4.80	8.18	5.24	4.14	2.37	–	93.70
chlorotrifluoromethane	1,3-dibromobenzene	12	4.89	4.89	4.82	4.82	4.89	4.82	5.21	4.72	4.93	6.41	–	148.17
chlorotrifluoromethane	*p*-xylene	8	3.48	3.48	4.33	4.33	3.48	4.33	6.94	3.35	3.03	1.15	–	95.55
cyclohexane	acetone	4	0.43	0.43	0.51	0.52	0.82	0.66	0.13	0.10	0.42	0.14	3.10	20.36
cyclohexane	argon	7	4.59	4.06	3.23	3.21	2.24	2.98	2.71	3.48	3.60	3.54	11.80	4.41
cyclohexane	benzene	12	8.55	8.59	8.79	8.76	9.06	9.03	6.20	2.45	8.04	3.04	6.07	18.74
cyclohexane	carbon tetrachloride	7	1.60	1.61	1.95	1.98	2.66	1.80	1.41	0.97	1.29	1.02	3.57	20.97
cyclohexane	1,1'-dimethylferrocene	5	0.81	0.91	0.91	0.81	0.33	0.34	5.44	5.43	0.96	5.90	3.07	8.87
cyclohexane	ethane	5	1.03	1.03	1.08	1.08	2.29	1.10	2.35	2.04	1.10	2.40	10.22	2.46
cyclohexane	ethylene	5	1.08	1.02	0.79	0.78	3.21	1.22	2.36	1.82	0.93	2.30	10.85	1.44
cyclohexane	ethylferrocene	6	0.80	0.87	0.89	0.82	0.54	0.56	0.97	0.97	0.88	1.30	1.19	7.74
cyclohexane	ferrocene	5	0.94	1.00	1.01	0.95	0.51	0.52	5.31	5.30	1.03	5.77	2.90	14.59

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
cyclohexane	krypton	6	1.71	1.50	1.19	1.18	0.68	1.08	0.93	1.27	1.53	1.26	10.23	15.74
cyclohexane	methane	6	1.36	1.25	1.02	1.01	0.64	0.92	0.32	0.73	1.16	0.68	7.38	9.52
cyclohexane	naphthalene	12	7.49	7.51	7.73	7.71	8.51	7.97	6.40	2.18	6.96	2.99	7.66	12.12
cyclohexane	phenanthrene	8	3.83	3.65	3.43	3.43	6.41	3.72	4.79	1.84	2.69	4.31	6.30	4.48
cyclohexane	tetrabutyltin	7	2.39	2.38	2.77	2.80	3.52	2.65	2.39	2.22	2.52	2.35	2.48	24.22
cyclohexane	tetraethyltin	7	1.95	1.93	2.04	2.05	3.66	2.01	2.33	1.89	1.93	2.16	2.90	24.31
cyclohexane	tetramethyltin	7	1.44	1.53	1.95	1.97	2.42	1.77	1.37	1.20	1.37	1.25	4.55	32.70
cyclohexane	tetrapropyltin	6	1.55	1.41	1.99	2.02	4.18	1.82	2.57	1.77	1.52	2.10	3.08	24.92
cyclohexane	toluene	12	7.27	7.29	7.48	7.45	8.61	7.72	6.33	2.28	6.79	2.85	7.90	11.74
cyclohexane	1,3,5-trimethylbenzene	12	7.79	7.88	8.18	8.15	10.11	8.42	7.25	3.02	7.55	2.42	6.82	13.51
cyclohexane	xenon	7	0.92	0.96	1.21	1.22	2.63	1.40	1.84	1.16	1.00	1.29	10.48	23.62
cyclohexane	*m*-xylene	4	1.29	1.28	1.21	1.21	1.24	1.21	1.49	1.52	1.29	1.52	5.18	21.96
cyclohexane	*p*-xylene	8	3.68	3.31	2.84	2.84	5.88	3.00	4.31	1.28	2.66	3.88	7.62	4.13
n-decane	12-crown-4	4	3.95	3.77	3.34	3.33	2.77	3.02	2.66	2.87	3.44	2.75	2.93	22.92
n-decane	15-crown-5	4	6.65	6.35	5.65	5.62	5.09	5.33	4.93	5.30	5.85	4.99	5.15	26.87
n-decane	18-crown-6	4	4.02	3.76	3.25	3.25	3.01	3.08	2.94	3.16	3.11	3.01	2.97	26.79
n-decane	dicyclohexano-18-crown-6	4	1.27	1.21	1.20	1.22	1.26	1.01	1.19	1.06	1.01	1.26	3.00	25.60
n-decane	dicyclohexano-24-crown-8	4	2.06	1.96	1.82	1.83	1.79	1.69	1.76	1.63	1.67	1.81	3.31	27.69
n-decane	tetrabutyltin	4	1.18	1.01	0.53	0.51	3.75	0.17	3.01	1.67	0.89	2.70	1.39	29.17
n-decane	tetramethyltin	4	1.66	1.28	0.30	0.30	2.75	0.61	2.27	1.09	1.19	1.91	1.31	37.07

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-decane	tetrapropyltin	4	1.70	1.44	0.66	0.62	3.02	0.26	2.40	1.13	1.29	2.07	0.24	29.18
n-decane	*s*-trioxane	4	0.91	0.79	0.35	0.32	0.69	0.03	0.61	0.24	0.74	0.64	1.36	24.60
n-decane	xenon	8	3.33	3.11	3.36	3.45	4.24	3.78	4.08	3.46	3.29	3.90	7.94	16.60
deuterium oxide	oxygen	18	6.49	5.93	3.92	3.87	4.24	3.67	2.24	2.22	5.24	2.28	–	18.03
2,3-dimethylbutane	benzene	11	1.71	1.71	1.76	1.78	2.44	2.46	0.64	0.99	1.67	1.56	1.65	13.55
2,3-dimethylbutane	naphthalene	9	1.81	1.81	1.82	1.82	2.84	2.86	0.77	0.95	1.76	1.75	2.07	18.87
2,3-dimethylbutane	phenanthrene	11	1.77	1.77	1.76	1.76	2.55	2.54	0.68	0.92	1.75	1.53	2.91	20.55
2,3-dimethylbutane	toluene	10	2.32	2.38	2.37	2.31	3.34	3.36	0.96	1.14	2.33	1.79	1.41	17.20
n-dodecane	acetone	5	1.22	1.22	1.19	1.19	1.19	1.16	1.21	1.20	1.20	1.29	1.02	4.74
n-dodecane	benzene	4	0.43	0.43	0.49	0.50	0.69	0.59	0.76	0.70	0.40	0.82	0.49	4.42
n-dodecane	carbon dioxide	9	4.48	3.39	1.13	1.21	3.71	1.73	2.54	1.49	3.62	1.49	8.37	79.44
n-dodecane	carbon monoxide	9	5.09	4.86	6.21	6.29	10.42	6.59	8.24	6.48	5.03	6.50	9.32	59.08
n-dodecane	*n*-decane	5	3.30	2.68	1.35	1.31	10.59	0.78	6.47	2.76	2.28	2.98	2.18	47.32
n-dodecane	*n*-hexadecane	5	2.73	1.99	1.97	1.97	15.93	1.51	10.05	5.72	1.92	6.69	4.43	58.94
n-dodecane	hydrogen	9	5.40	4.98	4.91	4.98	10.39	5.42	7.95	5.34	5.00	5.23	5.41	23.37
n-dodecane	linoleic acid methyl ester	4	0.37	0.38	0.44	0.44	0.34	0.39	0.36	0.33	0.39	0.40	2.24	13.54
n-dodecane	naphthalene	5	1.99	1.91	1.61	1.60	1.61	1.51	1.52	1.58	1.72	1.47	1.86	8.32
n-dodecane	*n*-cctane	9	4.68	3.45	1.94	1.88	6.52	1.55	4.01	1.04	3.04	1.48	1.47	48.89
n-dodecane	*n*-tetradecane	5	3.02	2.79	2.93	2.98	16.13	3.86	11.12	6.78	2.05	7.84	3.70	55.73
n-dodecane	toluene	4	1.06	1.07	1.18	1.19	1.41	1.29	1.47	1.41	1.04	1.54	1.16	9.74

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-dodecane	1,3,5-trimethylbenzene	4	1.33	1.30	1.12	1.10	1.01	1.02	0.93	0.98	1.27	0.87	1.54	4.35
n-dodecane	vitamin K_3	4	0.79	0.77	0.65	0.64	0.53	0.60	0.53	0.54	0.75	0.53	0.73	11.27
n-dodecane	*m*-xylene	4	0.62	0.64	0.79	0.81	0.95	0.89	1.02	0.96	0.62	1.08	1.15	10.17
n-eicosane	carbon dioxide	5	0.83	0.80	1.33	1.41	2.83	2.00	2.25	1.66	0.78	2.07	4.71	157.69
n-eicosane	carbon monoxide	5	0.65	0.82	1.69	1.81	3.66	2.45	2.69	1.92	0.61	2.43	2.88	128.01
n-eicosane	*n*-dodecane	5	1.25	1.28	1.51	1.54	5.09	2.15	4.45	3.43	1.06	4.28	2.29	136.14
n-eicosane	*n*-hexadecane	5	0.85	0.87	0.89	0.89	3.80	0.98	3.50	2.75	0.87	3.44	2.23	141.94
n-eicosane	hydrogen	5	2.94	2.79	3.32	3.42	6.06	4.08	4.85	3.96	2.24	4.65	3.44	8.42
n-eicosane	*n*-octane	5	2.38	2.42	2.88	2.94	6.10	3.61	4.95	4.01	2.26	4.78	3.11	130.52
ethane	1-octene	6	2.50	2.52	2.59	2.58	2.54	2.57	1.27	1.39	2.77	1.40	5.98	4.78
ethane	1-tetradecene	9	3.58	3.56	3.45	3.45	3.67	3.42	2.41	2.05	3.48	1.61	2.02	17.61
ethanol	ammonia	18	3.67	3.67	3.65	3.65	3.77	3.77	4.52	4.52	3.67	4.91	–	41.07
ethanol	benzene	21	10.35	7.10	1.90	1.67	3.62	2.03	7.68	5.52	8.90	15.89	–	25.50
ethanol	benzonitrile	16	0.86	0.91	0.94	0.90	0.76	0.77	1.75	1.75	0.89	1.75	–	25.16
ethanol	benzyl acetate	15	2.75	2.85	2.90	2.80	2.40	2.47	2.78	2.79	3.02	3.36	–	15.28
ethanol	1,2-butanediol	5	1.26	1.18	0.88	0.88	4.31	0.93	7.76	6.71	1.14	7.82	–	28.71
ethanol	1,4-butanediol	4	2.84	2.65	1.94	1.93	6.67	2.23	10.79	9.52	2.38	10.88	–	48.40
ethanol	1-butanol	4	1.67	1.41	1.00	1.00	2.31	1.01	6.12	5.05	1.04	6.05	–	17.42
ethanol	carbon dioxide	27	4.25	4.04	4.02	4.23	5.26	5.12	4.57	4.70	3.88	4.80	–	47.62
ethanol	dibenzyl ether	15	2.04	2.07	2.07	2.04	1.53	1.54	3.31	3.30	2.09	4.00	–	24.76

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
ethanol	ethylene glycol	5	2.34	2.39	2.46	2.46	4.01	2.47	7.08	6.15	2.42	7.08	–	59.15
ethanol	glycerol	5	3.28	2.95	1.56	1.54	6.76	1.79	10.18	9.07	2.41	10.35	–	52.51
ethanol	naphthalene	13	1.98	1.41	0.90	0.95	2.39	2.46	3.19	4.09	1.48	8.18	–	15.35
ethanol	nitrous oxide	5	0.68	0.56	0.22	0.20	0.40	0.18	0.16	0.18	0.58	0.16	–	44.94
ethanol	phenanthrene	13	1.37	1.14	1.09	1.23	3.22	3.23	3.52	3.60	1.01	4.86	–	10.25
ethanol	2-phenylethyl acetate	15	2.01	2.06	2.04	1.99	1.53	1.52	3.03	3.02	2.08	3.72	–	17.56
ethanol	3-phenylpropyl acetate	15	1.93	1.95	1.95	1.94	1.99	1.86	4.63	4.59	1.91	5.18	–	13.65
ethanol	propane	30	8.29	7.83	6.98	7.07	9.61	8.04	3.98	3.78	6.90	3.92	–	42.67
ethanol	propene	30	7.88	7.48	7.04	7.09	9.40	8.23	4.12	3.99	6.98	4.22	–	45.33
ethanol	toluene	14	2.30	1.69	1.14	0.88	2.76	2.13	2.63	4.53	1.95	8.99	–	19.00
ethanol	1,3,5-trimethylbenzene	13	1.69	1.28	1.82	1.66	2.48	2.50	3.84	4.21	1.28	8.04	–	16.75
ethanol	water	15	4.68	4.45	3.29	3.27	6.78	3.41	8.73	7.99	4.26	8.93	–	143.32
ethylene glycol	propene	31	1.63	1.67	2.73	2.85	3.49	3.45	2.23	2.10	1.68	2.57	–	48.85
n-heptane	benzene	11	2.46	2.45	2.45	2.45	2.43	2.45	2.44	2.44	2.46	2.44	2.36	5.54
n-heptane	*n*-decane	6	2.85	1.79	0.57	0.62	2.51	0.97	1.61	0.68	1.40	1.40	0.92	8.35
n-heptane	*n*-dodecane	6	2.46	2.05	1.43	1.40	2.62	1.28	2.20	1.39	2.00	1.64	1.24	9.20
n-heptane	ethylbenzene	4	0.23	0.21	0.17	0.17	0.17	0.17	0.17	0.17	0.22	0.17	0.82	8.27
n-heptane	*n*-hexadecane	9	1.38	1.11	1.03	1.03	3.95	1.23	3.19	1.00	1.18	0.87	1.91	5.55
n-heptane	*n*-hexane	11	1.20	1.20	1.21	1.21	1.35	1.21	1.30	1.25	1.20	1.30	1.39	9.59
n-heptane	*n*-octane	13	1.97	1.68	1.38	1.42	3.03	1.80	2.15	1.43	1.65	1.81	1.65	8.85

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-heptane	*n*-tetradecane	6	1.64	1.63	1.82	1.82	3.24	1.86	2.76	1.79	1.84	1.63	1.43	8.55
n-heptane	toluene	4	0.56	0.50	0.38	0.37	0.39	0.35	0.39	0.43	0.51	0.42	2.31	3.97
n-heptane	1,3,5-trimethylbenzene	4	0.73	0.70	0.62	0.61	0.53	0.59	0.56	0.61	0.70	0.58	0.68	4.72
n-heptane	2,2,4-trimethylpentane	4	0.38	0.38	0.37	0.37	0.35	0.37	0.36	0.37	0.38	0.36	0.43	2.12
n-heptane	*o*-xylene	4	0.30	0.24	0.12	0.11	0.15	0.10	0.14	0.18	0.25	0.17	3.24	4.78
n-heptane	*p*-xylene	4	0.67	0.62	0.50	0.49	0.49	0.47	0.50	0.54	0.62	0.53	2.10	6.75
n-hexadecane	carbon dioxide	10	5.35	3.92	0.42	0.60	3.04	1.84	0.98	3.01	3.41	2.97	4.14	104.85
n-hexadecane	carbon monoxide	10	4.64	3.50	3.36	3.61	6.76	4.68	3.60	3.01	3.13	2.92	3.31	88.11
n-hexadecane	*n*-decane	5	2.07	2.19	2.53	2.58	12.50	4.31	6.89	4.25	1.74	6.01	11.12	75.91
n-hexadecane	*n*-dodecane	5	2.72	2.04	0.79	0.80	8.15	2.21	3.61	1.44	1.52	2.43	4.88	75.79
n-hexadecane	hydrogen	10	10.43	7.96	3.86	3.62	4.80	2.95	5.98	7.40	8.11	7.77	6.40	22.87
n-hexadecane	*n*-octane	10	2.74	1.96	1.18	1.24	9.52	2.60	4.67	2.23	1.47	3.65	8.82	77.68
n-hexadecane	*n*-tetradecane	5	1.56	1.56	1.87	1.93	11.37	3.61	6.34	4.00	1.40	5.42	7.32	75.39
n-hexane	acetone	5	2.80	2.69	2.68	2.77	3.02	3.06	2.60	2.63	2.73	2.82	2.11	4.26
n-hexane	acetonitrile	7	2.70	2.70	2.31	2.31	2.70	2.31	8.77	7.30	2.37	5.93	5.82	5.79
n-hexane	benzene	48	7.77	6.29	6.89	6.96	41.09	8.45	28.80	12.64	6.44	14.03	4.83	7.22
n-hexane	carbon disulphide	10	4.36	4.36	4.35	4.35	4.36	4.35	7.82	6.20	4.49	4.66	4.76	7.03
n-hexane	carbon tetrabromide	8	7.39	7.39	2.14	2.14	7.39	2.14	20.38	18.46	5.38	16.42	5.89	20.90
n-hexane	*o*-difluorobenzene	7	3.73	3.15	2.14	2.09	2.85	1.90	2.66	2.09	2.90	2.81	1.78	11.81
n-hexane	*p*-difluorobenzene	7	4.33	3.50	2.01	1.94	0.67	1.30	0.52	0.92	3.13	0.75	1.30	13.99

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-hexane	9,10-dimethylanthracene	8	2.96	2.96	3.42	3.42	2.96	3.42	9.44	7.59	2.92	5.67	1.18	15.91
n-hexane	1,1'-dimethylferrocene	4	0.32	0.32	0.27	0.27	0.32	0.27	0.22	0.23	0.33	0.23	0.89	16.53
n-hexane	ethylferrocene	4	0.15	0.15	0.16	0.16	0.15	0.16	0.20	0.18	0.15	0.17	0.68	18.11
n-hexane	ferrocene	4	0.11	0.11	0.17	0.17	0.11	0.17	0.28	0.26	0.10	0.24	0.51	25.01
n-hexane	*n*-heptane	11	5.15	4.81	5.00	5.15	0.65	0.65	4.67	4.70	4.73	2.36	5.24	12.64
n-hexane	hexafluorobenzene	7	3.30	2.88	1.87	1.81	2.42	1.78	2.06	1.64	3.03	2.18	1.98	9.63
n-hexane	naphthalene	21	3.69	3.14	3.00	2.98	9.33	3.82	3.13	6.26	3.13	15.09	6.39	12.02
n-hexane	octafluorotoluene	7	3.15	2.69	1.74	1.73	2.40	1.63	2.12	1.51	2.55	2.26	1.89	10.36
n-hexane	*n*-octane	7	0.48	0.48	0.49	0.49	0.30	0.48	0.33	0.35	0.47	0.30	0.43	12.68
n-hexane	pentafluorobenzene	7	3.58	3.16	1.92	1.88	2.20	1.81	1.85	1.65	3.52	1.94	2.97	10.64
n-hexane	phenanthrene	15	5.27	4.48	3.37	3.37	8.24	4.87	2.81	5.90	3.80	11.81	6.54	14.18
n-hexane	pyrene	8	4.90	4.90	4.71	4.71	4.90	4.71	5.96	4.26	4.22	2.56	1.85	53.21
n-hexane	1,2,3,5-tetrafluorobenzene	7	4.04	3.62	2.78	2.73	3.14	2.58	2.75	2.36	3.55	2.83	2.67	18.29
n-hexane	1,2,4,5-tetrafluorobenzene	7	4.08	3.59	2.50	2.47	2.24	2.14	2.02	1.83	2.95	2.20	2.04	17.45
n-hexane	toluene	32	6.28	4.53	5.37	5.54	40.52	8.26	32.12	12.69	4.44	13.96	5.22	8.28
n-hexane	1,2,4-trifluorobenzene	7	2.26	1.61	0.79	0.79	2.42	1.05	2.08	1.25	1.27	2.20	2.24	17.57
n-hexane	1,3,5-trimethylbenzene	20	7.22	5.58	3.68	3.65	13.12	5.29	3.38	5.54	4.16	14.54	5.22	8.96
n-hexane	vitamin K_3	5	0.65	0.65	0.64	0.64	0.65	0.64	0.64	0.64	0.65	0.64	2.07	15.35
n-hexane	*m*-xylene	5	2.08	2.10	2.08	2.06	2.13	2.07	2.11	2.12	2.09	1.91	2.94	8.53
n-hexane	*p*-xylene	17	5.35	4.23	3.11	3.14	10.94	4.01	3.15	7.49	3.40	16.35	7.25	11.86

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
methanol	acetonitrile	26	1.85	2.19	2.01	1.63	1.40	1.46	7.60	7.37	2.29	8.70	–	26.98
methanol	ammonia	24	3.98	3.96	3.99	4.00	4.23	4.53	5.41	5.43	4.02	5.82	–	112.35
methanol	benzene	4	3.56	3.13	2.47	2.49	4.02	2.71	1.08	1.92	2.95	3.71	–	9.84
methanol	carbon dioxide	25	4.05	3.84	3.44	3.47	3.78	3.66	2.72	2.81	3.98	3.12	–	30.80
methanol	carbon monoxide	8	4.02	3.89	3.62	3.60	3.68	3.56	3.70	3.79	4.17	3.79	–	15.85
methanol	*p*-chloronitrobenzene	18	0.98	1.00	1.00	0.98	0.76	0.78	0.69	0.71	1.03	0.94	–	22.58
methanol	naphthalene	4	3.68	3.25	2.55	2.57	4.02	2.79	0.97	2.06	3.06	3.86	–	16.79
methanol	phenanthrene	4	2.93	2.70	2.38	2.40	4.95	2.62	2.21	0.91	2.47	2.65	–	19.00
methanol	propane	27	2.46	2.38	2.16	2.11	2.22	2.06	2.34	2.27	2.50	2.55	–	25.81
methanol	toluene	4	3.66	3.03	2.07	2.09	2.94	2.31	0.19	2.74	3.04	4.57	–	14.12
methanol	1,3,5-trimethylbenzene	4	3.25	2.87	2.28	2.31	4.14	2.52	1.37	1.67	2.66	3.45	–	15.85
methanol	water	5	1.74	1.73	1.77	1.77	1.69	1.77	1.72	1.73	1.69	1.72	–	292.95
methanol	[Bmim][bti]	11	3.58	3.59	3.65	3.64	3.37	3.59	3.50	3.55	3.75	3.49	–	42.07
methanol	[Emim][bti]	11	2.87	2.88	2.92	2.92	2.78	2.87	2.81	2.83	2.97	2.81	–	41.27
methanol	[Hmim][bti]	5	1.32	1.31	1.31	1.31	1.76	1.37	1.47	1.39	1.25	1.49	–	38.05
methanol	[Omim][bti]	5	1.33	1.32	1.30	1.30	1.27	1.30	1.32	1.32	1.28	1.30	–	39.02
n-octacosane	carbon dioxide	5	2.63	2.11	2.20	2.31	3.51	2.90	2.12	1.63	1.70	2.08	18.97	173.15
n-octacosane	carbon monoxide	5	3.22	2.79	3.54	3.64	5.39	4.11	3.81	3.26	2.93	3.79	15.47	131.14
n-octacosane	*n*-dodecane	5	1.87	1.80	1.88	1.89	6.58	3.01	3.72	2.74	1.73	3.77	12.85	183.91
n-octacosane	*n*-hexadecane	5	2.45	2.13	1.88	1.88	7.34	3.00	4.32	3.18	1.77	4.40	14.89	200.39

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-octacosane	hydrogen	5	1.18	1.45	2.81	3.07	4.01	4.01	2.36	1.81	1.32	2.26	18.43	12.28
n-octacosane	*n*-octane	5	1.08	1.05	1.15	1.17	5.13	1.83	2.61	1.83	1.06	2.65	13.96	166.97
n-octane	argon	4	1.50	1.17	0.29	0.19	0.65	0.27	1.84	2.42	1.04	2.62	3.48	12.24
n-octane	benzene	8	0.24	0.23	0.22	0.22	0.21	0.22	0.22	0.22	0.23	0.22	1.35	2.85
n-octane	carbon tetrachloride	4	1.05	0.95	0.69	0.68	0.57	0.55	0.51	0.61	0.88	0.52	0.76	15.76
n-octane	ethylbenzene	8	1.43	1.46	1.55	1.56	1.65	1.61	1.59	1.54	1.44	1.58	1.82	5.43
n-octane	*n*-heptane	7	1.05	1.05	1.06	1.05	0.89	0.98	0.89	0.93	1.13	0.88	0.95	11.50
n-octane	*n*-hexane	6	1.10	1.09	1.09	1.10	0.69	1.02	0.83	0.92	1.00	0.82	2.78	5.96
n-octane	krypton	4	1.40	1.21	0.78	0.79	1.03	0.83	1.75	2.36	1.28	2.53	4.29	28.16
n-octane	methane	4	1.27	1.06	0.43	0.37	1.13	0.17	1.80	2.47	0.93	2.60	1.95	5.12
n-octane	tetrabutyltin	4	7.64	6.27	4.36	4.50	6.04	5.25	1.85	1.02	6.18	1.28	3.47	30.13
n-octane	tetraethyltin	5	3.79	3.70	3.80	3.70	3.20	3.28	6.79	6.21	3.88	6.60	4.66	34.09
n-octane	tetramethyltin	4	8.09	6.75	4.74	4.95	6.39	5.64	0.35	1.12	7.25	1.01	0.96	44.76
n-octane	tetrapropyltin	4	8.07	6.89	5.12	5.28	6.49	6.01	0.67	0.85	7.17	0.72	2.19	32.17
n-octane	1,3,5-trimethylbenzene	8	0.48	0.48	0.50	0.50	0.57	0.52	0.54	0.52	0.50	0.54	0.64	7.07
n-octane	toluene	8	1.38	1.41	1.51	1.52	1.60	1.56	1.54	1.49	1.39	1.53	1.55	2.85
n-octane	xenon	8	5.03	4.95	5.48	5.56	5.87	5.79	4.63	4.63	4.92	4.70	9.14	17.27
n-octane	*o*-xylene	8	0.73	0.74	0.75	0.75	1.00	0.80	0.90	0.84	0.72	0.91	1.02	1.30
n-octane	*p*-xylene	8	0.84	0.83	0.81	0.81	0.92	0.83	0.87	0.85	0.80	0.88	1.32	8.89
propane	1-octene	8	1.47	1.42	1.55	1.65	2.30	2.30	1.68	1.52	1.43	1.65	2.23	19.38

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
propane	1-tetradecene	8	1.86	1.84	1.82	1.80	1.80	1.80	1.83	1.83	1.85	1.85	2.61	30.56
1-propanol	ammonia	31	2.84	2.81	2.89	2.88	2.86	2.84	7.90	7.66	2.83	8.35	–	45.10
1-propanol	carbon dioxide	27	2.74	2.27	1.47	1.44	2.24	1.46	3.03	2.93	2.49	3.35	–	51.79
1-propanol	propane	36	5.28	4.84	3.68	3.70	4.85	3.76	3.45	3.38	4.66	3.73	–	47.31
1-propanol	propene	36	4.55	4.11	3.05	3.00	4.06	2.98	3.15	3.07	4.27	3.49	–	50.55
1-propanol	water	5	3.01	3.00	3.16	3.17	2.31	3.12	2.53	2.51	2.56	2.57	–	155.26
2-propanol	benzene	10	8.05	6.56	3.74	3.86	7.21	4.81	6.82	7.06	4.60	10.91	–	10.57
2-propanol	*n*-decane	10	12.74	9.48	3.70	3.77	8.44	4.18	8.26	5.25	5.76	9.01	–	17.82
2-propanol	naphthalene	10	8.88	7.08	3.65	3.85	7.88	4.74	6.54	7.83	5.40	12.24	–	11.40
2-propanol	phenanthrene	9	10.20	8.36	4.19	4.30	8.40	4.89	4.69	5.19	6.26	8.89	–	11.59
2-propanol	*n*-tetradecane	9	9.33	7.83	4.28	4.38	7.68	5.08	7.31	6.75	5.06	10.34	–	15.19
2-propanol	toluene	10	7.54	6.06	3.18	3.31	6.45	4.15	6.48	6.86	4.49	10.62	–	10.78
2-propanol	water	5	1.19	1.19	1.25	1.25	1.66	1.29	4.91	4.61	1.20	4.96	–	140.59
sulfur hexafluoride	benzene	9	6.33	6.33	2.78	2.78	6.33	2.78	18.04	5.53	4.26	10.58	8.41	86.19
sulfur hexafluoride	benzoic acid	6	1.90	1.91	1.87	1.87	2.98	2.88	3.88	2.92	1.83	2.61	4.99	147.43
sulfur hexafluoride	carbon tetrachloride	6	2.05	2.05	0.88	0.88	2.05	0.88	10.51	3.11	2.21	5.18	3.18	128.35
sulfur hexafluoride	naphthalene	5	2.44	2.55	2.38	2.28	3.37	3.08	6.84	5.94	2.81	5.52	5.47	69.85
sulfur hexafluoride	toluene	11	4.17	4.17	2.43	2.43	4.17	2.43	12.89	3.64	3.16	9.73	11.39	85.20
sulfur hexafluoride	1,3,5-trimethylbenzene	10	4.43	4.43	4.13	4.13	4.43	4.13	8.17	4.58	4.08	4.59	10.37	90.68
sulfur hexafluoride	*p*-xylene	52	3.93	4.06	4.56	4.37	5.43	6.56	11.51	3.77	3.89	12.41	7.57	88.40

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
n-tetradecane	acridine	8	5.20	4.42	3.94	3.98	4.05	4.13	4.88	4.44	4.05	4.76	23.62	22.74
n-tetradecane	benzothiophene	7	2.87	2.80	2.46	2.44	3.54	2.42	3.20	2.73	2.83	3.18	17.85	39.25
n-tetradecane	dibenzothiophene	8	5.32	4.98	4.32	4.35	7.44	4.52	6.53	6.00	3.82	6.76	15.01	37.06
n-tetradecane	naphthalene	7	2.67	2.68	3.14	3.23	5.53	3.79	4.93	4.17	2.43	5.12	26.52	14.51
n-tetradecane	xenon	4	0.39	0.42	0.72	0.75	0.61	0.84	0.94	0.88	0.43	1.04	22.02	10.06
2,2,4-trimethylpentane	benzene	4	1.55	1.52	1.44	1.44	1.39	1.38	1.59	1.63	1.46	1.62	2.43	4.81
2,2,4-trimethylpentane	ethylbenzene	4	1.20	1.18	1.07	1.05	0.90	0.93	1.31	1.36	1.16	1.34	1.41	9.70
2,2,4-trimethylpentane	toluene	4	1.45	1.43	1.34	1.32	1.14	1.20	1.57	1.63	1.41	1.59	1.71	1.79
2,2,4-trimethylpentane	1,3,5-trimethylbenzene	4	0.86	0.85	0.82	0.82	1.05	0.85	0.83	0.82	0.83	0.84	5.03	11.73
2,2,4-trimethylpentane	*o*-xylene	4	2.08	2.06	2.02	2.02	1.73	1.89	2.23	2.29	2.03	2.25	3.06	6.81
2,2,4-trimethylpentane	*p*-xylene	4	1.89	1.89	1.84	1.82	1.76	1.76	1.94	1.96	1.95	1.95	1.85	5.32
water	acetamide	4	1.94	1.96	2.01	2.01	2.21	2.01	8.19	8.22	2.09	8.37	–	7.43
water	acetone	4	1.20	1.17	1.07	1.07	1.13	1.07	1.64	1.65	1.21	1.66	–	6.28
water	alanine	6	0.42	0.42	0.44	0.44	1.06	0.59	1.61	1.66	0.45	1.56	–	28.16
water	alloisoleucine	6	0.07	0.08	0.15	0.16	0.68	0.10	1.95	2.00	0.08	1.88	–	2.49
water	allothreonine	6	0.22	0.22	0.20	0.19	0.92	0.35	1.74	1.80	0.25	1.68	–	12.34
water	aluminium chloride	5	0.48	0.47	0.37	0.36	0.72	0.43	0.32	0.32	0.46	0.30	–	–
water	ammonia	5	0.91	0.86	0.68	0.67	0.66	0.65	2.45	2.49	0.81	2.43	–	36.59
water	arabinose	6	1.34	1.23	0.85	0.84	5.25	1.76	11.92	12.07	0.85	12.22	–	4.11
water	argon	8	1.40	1.40	1.58	1.60	1.97	1.78	6.12	6.14	1.31	6.47	–	50.62

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	barium chloride	5	1.08	1.07	0.97	0.97	0.93	0.93	1.51	1.52	1.00	1.51	–	–
water	benzene	24	1.98	1.93	1.79	1.80	5.64	2.24	9.39	9.64	1.73	9.46	–	11.04
water	benzoic acid	12	2.28	2.24	2.10	2.09	3.53	2.39	2.77	2.84	2.25	2.70	–	15.72
water	beryllium chloride	5	0.58	0.58	0.61	0.61	0.68	0.64	0.59	0.59	0.58	0.58	–	–
water	biphenyl	7	0.93	0.82	0.69	0.69	5.42	1.21	8.88	9.20	0.70	8.84	–	19.85
water	*n*-butane	16	12.03	11.41	8.95	8.95	13.29	9.21	9.77	9.77	9.21	9.89	–	11.19
water	1,2-butanediol	5	0.62	0.51	0.54	0.56	6.24	0.90	11.68	11.99	0.38	11.67	–	2.19
water	1,3-butanediol	5	0.11	0.12	0.17	0.17	1.06	0.14	2.25	2.34	0.10	2.14	–	8.11
water	1,4-butanediol	5	1.54	1.39	0.79	0.77	7.13	1.63	10.86	11.17	1.09	10.83	–	2.28
water	1-butanol	13	4.89	4.52	3.54	3.53	9.33	3.90	9.35	9.62	3.56	9.31	–	3.81
water	2-methyl-1-butanol	6	2.72	2.53	1.31	1.26	7.15	2.19	11.81	11.97	2.16	12.05	–	6.51
water	3-methyl-1-butanol	6	1.99	1.88	1.02	0.97	6.29	1.90	12.35	12.51	1.79	12.61	–	4.72
water	2-methyl-2-butanol	6	2.44	2.24	0.87	0.81	6.98	1.75	12.53	12.69	2.02	12.76	–	4.13
water	3-methyl-2-butanol	6	2.55	2.28	0.91	0.87	6.85	1.69	12.37	12.54	1.80	12.62	–	5.32
water	*n*-butylbenzene	7	1.49	1.33	0.53	0.52	6.29	1.15	8.93	9.27	1.15	8.84	–	15.23
water	α-amino-*n*-butyric acid	6	0.26	0.26	0.27	0.27	0.79	0.33	1.80	1.85	0.26	1.74	–	9.32
water	caffeine	22	0.93	0.92	0.86	0.86	1.01	0.82	2.40	2.46	0.88	2.35	–	10.24
water	calcium chloride	5	0.12	0.12	0.12	0.12	0.27	0.17	0.62	0.63	0.12	0.60	–	–
water	camphor	8	1.20	1.18	1.15	1.15	1.08	1.09	3.81	3.84	1.15	3.84	–	14.43
water	carbon dioxide	111	4.61	4.39	3.78	3.78	6.28	4.01	5.33	5.39	3.75	5.36	–	3.74

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	cesium chloride	5	2.62	2.61	2.67	2.67	2.38	2.61	3.33	3.35	2.56	3.31	–	–
water	cinnamic acid	8	1.84	1.81	1.37	1.35	2.38	1.50	3.18	3.21	1.79	3.15	–	27.64
water	α-cyclodextrin	4	1.56	1.57	1.60	1.60	1.57	1.60	1.64	1.64	1.61	1.63	–	14.35
water	β-cyclodextrin	4	2.24	2.23	2.20	2.20	2.12	2.16	2.64	2.65	2.18	2.64	–	17.31
water	cyclohexane	10	6.09	6.10	6.11	6.11	6.02	6.14	10.14	10.22	6.20	10.39	–	7.11
water	cyclopentane	10	4.00	3.98	4.13	4.14	4.96	4.39	7.75	7.84	3.87	7.95	–	4.38
water	diethanolamine	5	1.51	1.47	1.31	1.31	0.79	1.27	2.27	2.36	1.45	2.21	–	2.00
water	diethylene glycol	5	0.97	0.97	0.97	0.97	1.03	0.99	0.80	0.80	0.94	0.80	–	2.86
water	*N*,*N*-diethylethanolamine	5	0.78	0.77	0.72	0.72	0.95	0.79	2.00	2.07	0.76	2.08	–	3.22
water	diglycolamine	5	0.44	0.46	0.61	0.62	1.12	0.79	0.73	0.79	0.49	0.68	–	7.44
water	diisopropanolamine	5	3.21	3.19	3.17	3.17	3.50	3.21	3.14	3.18	3.25	3.08	–	3.51
water	dimethylethanolamine	5	1.45	1.42	1.26	1.26	1.08	1.22	3.07	3.13	1.52	3.18	–	18.36
water	dipropylene glycol	5	0.59	0.60	0.70	0.71	0.69	0.75	0.58	0.58	0.63	0.57	–	3.28
water	*meso*-erythritol	5	0.96	0.93	0.68	0.68	6.21	1.43	11.14	11.43	0.87	11.15	–	9.36
water	ethane	16	3.84	3.82	3.50	3.51	3.31	3.46	8.89	8.93	3.46	9.04	–	7.15
water	ethanol	22	2.71	2.71	2.65	2.64	3.33	2.73	4.59	4.70	2.66	4.57	–	10.84
water	ethylbenzene	16	3.08	3.06	2.86	2.84	4.31	2.64	10.63	10.87	3.01	10.85	–	9.52
water	ethylene glycol	9	2.32	2.31	2.40	2.40	3.10	2.57	1.85	1.89	2.42	1.81	–	13.69
water	1-ethylnaphthalene	7	1.41	1.26	0.95	0.95	5.63	1.35	9.13	9.39	1.11	9.10	–	16.37
water	formamide	4	2.17	2.15	2.19	2.19	1.50	1.95	8.81	8.83	2.03	9.03	–	17.85

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	fructose	4	0.57	0.58	0.61	0.61	0.68	0.64	0.40	0.39	0.57	0.40	–	23.17
water	furfural	7	1.19	1.18	1.16	1.16	0.88	1.00	2.79	2.90	1.23	2.72	–	9.20
water	5-(hydroxymethyl) furfural	7	0.57	0.57	0.62	0.62	0.87	0.38	2.47	2.56	0.62	2.37	–	7.87
water	galactose	6	1.42	1.30	0.84	0.83	5.15	1.50	12.46	12.61	0.92	12.76	–	1.18
water	gallium chloride	5	1.72	1.66	1.05	1.03	2.04	1.09	0.93	0.91	1.61	0.99	–	–
water	glucose	10	2.10	2.01	1.74	1.73	5.23	2.20	8.03	8.13	1.81	8.22	–	10.02
water	glycerol	10	2.03	1.98	1.84	1.85	2.40	1.59	7.36	7.50	1.77	7.37	–	6.57
water	glycine	6	0.46	0.45	0.40	0.40	0.59	0.42	2.09	2.14	0.43	2.04	–	2.85
water	guaiacol	7	0.30	0.29	0.22	0.22	1.50	0.42	1.90	2.01	0.27	1.79	–	8.72
water	hexafluorobenzene	6	1.89	1.86	1.92	1.94	1.30	1.54	4.26	4.42	1.68	4.16	–	4.55
water	1,2,6-hexanetriol	5	2.48	2.44	2.38	2.38	3.13	2.54	2.37	2.42	2.35	2.32	–	1.66
water	homoserine	6	0.42	0.42	0.42	0.42	1.09	0.55	1.71	1.75	0.44	1.66	–	6.55
water	hydrogen	6	0.06	0.09	0.35	0.37	0.36	0.45	1.79	1.80	0.09	1.86	–	52.92
water	hydrogen sulfide	22	3.78	3.56	2.96	2.95	3.08	2.94	5.62	5.75	3.21	5.75	–	8.41
water	*myo*-inositol	5	2.22	1.95	0.85	0.81	7.81	2.08	10.37	10.68	1.39	10.32	–	8.28
water	isobutyramide	4	1.24	1.26	2.43	2.50	1.11	2.19	10.25	10.28	1.05	10.39	–	10.33
water	isoleucine	6	0.38	0.37	0.35	0.35	1.06	0.43	1.70	1.75	0.36	1.63	–	2.12
water	krypton	6	0.63	0.63	0.61	0.61	1.01	0.71	1.86	1.87	0.65	1.90	–	6.33
water	lactose	5	1.06	1.04	0.94	0.94	0.90	0.88	1.63	1.64	1.01	1.62	–	1.73
water	leucine	6	0.67	0.68	0.68	0.69	0.96	0.65	1.74	1.79	0.67	1.69	–	2.83

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	*tert*-leucine	6	0.53	0.54	0.59	0.60	0.67	0.50	2.25	2.31	0.52	2.18	–	4.10
water	lithium chloride	5	0.66	0.66	0.66	0.66	0.77	0.69	0.61	0.62	0.65	0.60	–	–
water	magnesium chloride	5	0.28	0.28	0.28	0.28	0.38	0.30	0.67	0.68	0.28	0.65	–	–
water	mannitol	5	1.86	1.78	1.30	1.29	6.93	2.16	10.77	11.07	1.71	10.76	–	5.35
water	mannose	6	2.10	2.06	1.74	1.74	5.46	2.62	11.93	12.08	1.83	12.23	–	1.81
water	methane	32	5.27	5.23	5.13	5.15	5.83	5.33	5.68	5.71	4.85	5.73	–	7.89
water	methanol	15	4.71	4.72	4.75	4.75	4.89	4.72	6.71	6.80	4.75	6.69	–	6.02
water	methyl bromide	6	3.96	3.85	2.98	2.97	4.37	3.07	1.86	1.86	3.31	1.90	–	5.26
water	methyl chloride	6	3.45	3.38	2.46	2.42	3.96	2.56	1.48	1.49	3.22	1.49	–	10.40
water	methylcyclopentane	10	2.00	1.94	2.00	2.00	2.45	1.98	10.24	10.32	2.10	10.50	–	4.36
water	*n*-methyldiethanolamine	5	1.82	1.75	1.49	1.49	1.06	1.50	2.32	2.40	1.49	2.26	–	2.41
water	methyl fluoride	6	1.89	1.83	0.77	0.74	2.40	0.82	2.20	2.22	1.89	2.14	–	8.93
water	*N*-methylpyrrolidone	5	0.18	0.18	0.14	0.13	0.94	0.21	2.22	2.31	0.20	2.13	–	4.59
water	monoethanolamine	9	3.97	3.95	3.78	3.76	3.66	3.65	4.37	4.44	3.94	4.49	–	4.46
water	monoisopropanolamine	5	2.12	2.12	2.16	2.17	2.72	2.25	0.70	0.69	2.03	0.73	–	12.21
water	naphthalene	7	0.79	0.73	0.58	0.57	5.26	1.11	8.86	9.18	0.70	8.83	–	20.42
water	2-naphthol	16	3.60	3.44	3.28	3.28	5.66	3.61	4.06	4.20	3.24	3.97	–	28.55
water	neon	6	0.07	0.04	0.30	0.32	0.21	0.40	1.72	1.73	0.03	1.81	–	21.76
water	nitrous oxide	78	8.23	8.10	7.61	7.58	9.52	7.75	7.18	7.19	7.95	7.19	–	8.77
water	norleucine	6	0.45	0.45	0.43	0.43	0.99	0.49	1.64	1.69	0.43	1.57	–	1.97

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	norvaline	6	0.33	0.33	0.26	0.25	1.00	0.41	1.63	1.69	0.34	1.56	–	5.74
water	oxygen	34	2.09	1.98	1.60	1.58	1.68	1.49	5.75	5.90	1.99	5.76	–	18.28
water	pentaerythritol	6	1.36	1.28	1.09	1.09	4.29	1.19	10.21	10.48	1.08	10.25	–	2.71
water	*n*-pentane	8	0.84	0.85	1.78	1.86	2.31	1.22	11.89	12.00	0.70	12.01	–	8.36
water	2-methyl-2,4-pentanediol	5	0.19	0.18	0.10	0.11	1.37	0.29	2.06	2.15	0.17	1.94	–	1.98
water	1-pentanol	6	2.59	2.46	1.44	1.39	6.72	2.32	12.20	12.35	2.35	12.44	–	6.94
water	2-pentanol	6	1.40	1.26	0.67	0.68	5.35	1.16	13.35	13.51	0.96	13.64	–	5.36
water	3-pentanol	6	2.35	2.10	0.78	0.74	6.74	1.62	12.48	12.64	1.73	12.73	–	4.97
water	phenol	17	3.35	3.23	2.86	2.83	27.77	4.45	21.69	29.78	3.16	41.77	–	9.96
water	piperazine	5	1.42	1.37	1.18	1.18	1.11	1.15	2.92	2.98	1.47	3.03	–	13.89
water	2-piperidineethanol	5	0.35	0.35	0.34	0.34	0.49	0.23	1.63	1.69	0.33	1.56	–	3.33
water	poly(ethylene glycol) 200	4	0.84	0.84	0.82	0.82	0.90	0.84	0.68	0.68	0.81	0.69	–	–
water	poly(ethylene glycol) 300	4	1.06	1.05	1.00	1.00	0.94	0.96	1.36	1.37	1.04	1.36	–	–
water	poly(ethylene glycol) 400	4	0.90	0.91	0.95	0.95	1.02	0.98	0.59	0.58	0.90	0.60	–	–
water	poly(ethylene glycol) 600	4	0.80	0.81	0.83	0.83	0.81	0.83	0.89	0.89	0.83	0.90	–	–
water	poly(propylene glycol) 400	4	0.67	0.67	0.67	0.67	0.74	0.69	0.53	0.53	0.68	0.53	–	–
water	potassium chloride	30	2.60	2.47	2.25	2.34	4.72	3.02	21.14	20.91	2.37	24.27	–	–
water	propanamide	4	2.37	2.34	2.64	2.70	1.90	2.48	10.28	10.31	1.99	10.44	–	10.72
water	propane	16	5.90	5.62	4.81	4.80	7.23	4.83	8.92	8.96	5.02	9.03	–	7.84
water	1-propanol	15	2.84	2.83	2.80	2.80	6.10	3.21	9.62	9.88	2.82	9.66	–	6.67

Table 2. (*Continued*)

System			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	TLSM$_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)	NDP	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	2,2-dimethyl-1-propanol	6	1.50	1.39	0.45	0.43	5.90	1.31	12.91	13.07	1.31	13.18	–	5.26
water	2-amino-2-methyl-1-propanol	5	0.82	0.83	0.87	0.88	1.19	0.97	1.35	1.39	0.82	1.30	–	6.91
water	2-propanol	12	4.84	4.85	4.61	4.62	5.55	4.57	9.45	9.57	4.56	9.52	–	7.63
water	2-methyl-2-propanol	9	3.12	3.13	3.29	3.31	5.22	2.92	11.38	11.68	3.01	11.38	–	7.12
water	propylene glycol	5	0.87	0.87	0.88	0.88	1.01	0.91	0.63	0.63	0.86	0.64	–	9.24
water	radon	6	1.07	1.04	0.63	0.61	1.51	0.74	1.93	1.95	0.99	1.94	–	14.03
water	rubidium chloride	5	0.32	0.32	0.30	0.30	0.21	0.25	0.88	0.90	0.33	0.87	–	–
water	salicylic acid	13	2.23	2.14	1.85	1.84	3.65	2.07	3.19	3.24	1.89	3.16	–	24.96
water	serine	6	0.29	0.28	0.27	0.27	1.01	0.45	1.58	1.64	0.26	1.53	–	13.69
water	sodium chloride	5	1.42	1.42	1.46	1.46	1.59	1.51	1.11	1.10	1.47	1.11	–	–
water	strontium chloride	5	0.84	0.84	0.77	0.77	0.65	0.71	1.44	1.45	0.82	1.43	–	–
water	sucrose	10	2.31	2.25	1.95	1.95	4.99	2.34	8.63	8.74	1.94	8.82	–	6.14
water	sulfolane	5	0.73	0.70	0.58	0.58	0.44	0.55	2.54	2.60	0.74	2.63	–	7.56
water	sulfur dioxide	4	0.15	0.15	0.17	0.17	0.27	0.21	0.50	0.51	0.15	0.50	–	10.51
water	tetraethylene glycol	5	0.69	0.69	0.71	0.71	0.78	0.74	0.65	0.65	0.69	0.64	–	2.31
water	threonine	6	0.33	0.33	0.34	0.34	0.90	0.39	1.83	1.88	0.33	1.78	–	15.44
water	toluene	15	2.31	2.18	2.31	2.32	3.34	1.83	12.14	12.42	2.14	12.32	–	6.36
water	triethanolamine	5	0.41	0.39	0.31	0.31	0.37	0.20	1.58	1.64	0.33	1.51	–	0.52
water	triethylene glycol	5	0.37	0.37	0.40	0.41	0.43	0.43	0.53	0.54	0.37	0.53	–	5.38
water	valine	6	0.22	0.21	0.20	0.20	0.79	0.26	1.87	1.92	0.21	1.80	–	6.27

Table 2. (*Continued*)

System		NDP	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)	Dymond (Eq. (12))	$TLSM_d$ (Eqs. (14) – (21))	Wilke - Chang (Eq. (13))
Solvent (1)	Solute (2)		AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD	AARD
water	vanillin	7	0.25	0.24	0.27	0.27	1.29	0.26	2.18	2.30	0.24	2.07	–	8.38
water	xenon	6	0.87	0.85	0.67	0.66	1.28	0.77	1.86	1.87	0.86	1.88	–	13.72
water	xylitol	5	1.73	1.65	1.36	1.34	6.73	2.21	10.60	10.89	1.58	10.60	–	2.21
water	xylose	6	0.77	0.72	0.53	0.53	4.77	1.27	12.50	12.65	0.61	12.82	–	2.85
water	[Bmim][BF_4]	11	1.22	1.18	0.98	0.97	1.13	1.00	3.64	3.68	1.16	3.67	–	49.02
water	[Bmim][bti]	18	4.64	4.58	4.35	4.35	4.24	4.31	6.34	6.38	4.47	6.39	–	50.31
water	[Bmim][CF_3SO_3]	5	1.61	1.58	1.40	1.39	1.49	1.37	1.85	1.86	1.56	1.87	–	38.09
water	[Bmim][Cl]	6	0.77	0.80	1.24	1.26	1.80	1.57	3.61	3.67	0.88	3.66	–	47.14
water	[Bmim][$MeSO_4$]	5	1.16	1.20	1.37	1.39	1.27	1.42	0.97	0.96	1.19	0.94	–	42.16
water	[Bmim][$OcSO_4$]	6	4.30	4.28	4.13	4.13	4.11	4.07	5.16	5.17	4.15	5.18	–	51.51
water	[Bmim][PF_6]	5	1.21	1.21	1.25	1.25	1.34	1.26	1.15	1.15	1.25	1.16	–	51.83
water	[Emim][BF_4]	5	1.30	1.33	1.49	1.50	1.41	1.53	1.10	1.10	1.39	1.10	–	46.75
water	[Emim][bti]	18	4.28	4.22	3.91	3.90	3.75	3.77	6.03	6.06	4.00	6.07	–	49.49
water	[Emim][$C_2H_5SO_4$]	11	3.09	3.07	2.97	2.97	2.95	2.94	4.06	4.08	3.04	4.08	–	42.67
water	[Emim][C_2N_3]	5	0.53	0.53	0.48	0.48	0.44	0.45	0.83	0.84	0.52	0.82	–	44.06
water	[Emim][CF_3SO_3]	5	1.65	1.64	1.69	1.69	1.60	1.68	2.02	2.03	1.69	2.00	–	43.45
water	[Emim][$MDEGSO_4$]	5	2.59	2.59	2.61	2.61	2.68	2.64	2.35	2.34	2.58	2.35	–	43.83
water	[Hmim][bti]	6	1.11	1.12	1.34	1.37	1.57	1.60	3.89	3.95	1.03	3.96	–	49.59
water	[Omim][bti]	6	1.74	1.68	1.60	1.62	1.74	1.67	4.44	4.49	1.63	4.55	–	49.86

Table 3 presents the global deviations achieved by our correlations, together with those found for the reference models of Dymond (2-parameters), TSLM_d (1-parameter), and Wilke-Chang (0-parameters). In the whole, the correlations presented perform accurately, with global AARDs between 2.78% (Eq. (4)) and 4.44% (Eq. (6)). It must be emphasized that our database includes systems composed of extremely different molecules: symmetrical and asymmetrical, polar and non-polar, small and large, light and heavy. One may check it comprehends 202 systems with water and alcohols (hydrogen--bonding solvents), the homologous series of alkanes (between C5 to C14) in supercritical CO_2, 15 systems of distinct ionic liquids in water (namely, [Bmim][BF_4], [Bmim][bti], [Bmim][CF_3SO_3], [Bmim][Cl], [Bmim][$MeSO_4$], [Bmim][$OcSO_4$], [Bmim][PF_6], [Emim][BF_4], [Emim][bti], [Emim][$C_2H_5SO_4$], [Emim][C_2N_3], [Emim][CF_3SO_3], [Emim][$MDEGSO_4$], [Hmim][bti], and [Omim][bti]), and various supercritical systems with organometallic solutes (*e.g.*, compounds with Co, Fe, Pd, Cu, Na).

Table 3. Global deviations (AARD, %) achieved by the equations studied in this work (see Table 1) and by the models adopted for comparison. The prediction ability of the new equations is also shown.

			Models analysed in this work									Models for comparison		
	NS	NDP	Eq.(1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq.(6)	Eq.(7)	Eq.(8)	Eq.(9)	Dymond	TLSM_d	Wilke-Chang
Correlation	539	8219	3.23	3.05	2.78	2.86	4.44	3.51	4.15	3.63	2.97	4.56	4.27	20.00
Prediction	539	7141*	4.46	4.41	4.24	4.21	6.04	5.32	5.99	5.57	4.44			

NS = number of systems; NDP = number of experimental data points; AARD = average absolute relative deviation. *Number of NDP involved in prediction.

Concerning the models selected for comparison, the global error for the 2-parameter free-volume equation of Dymond is 4.56%, for the 1-parameter TLSM_d model is 4.27%, and for the predictive Wilke-Chang expression is 20.00% (see Table 3). Despite possessing the same number of parameters, the grand AARDs of all new correlations are lower than that of Dymond. The TLSM_d model offered 4.27% with only one adjustable parameter, but it is a much lengthier equation. Remember that the main objective of this essay is to propose and/or analyse very simple and accurate correlations for the estimation of tracer diffusion coefficients for the generality of dense binary systems.

In order to reinforce the accuracy of the simple correlations presented (Table 1), calculated *versus* experimental diffusivity plots were drawn. In Figures 1.a and 1.b the results for Eqs. (4) and (9) are shown. Very similar plots were obtained for the remaining

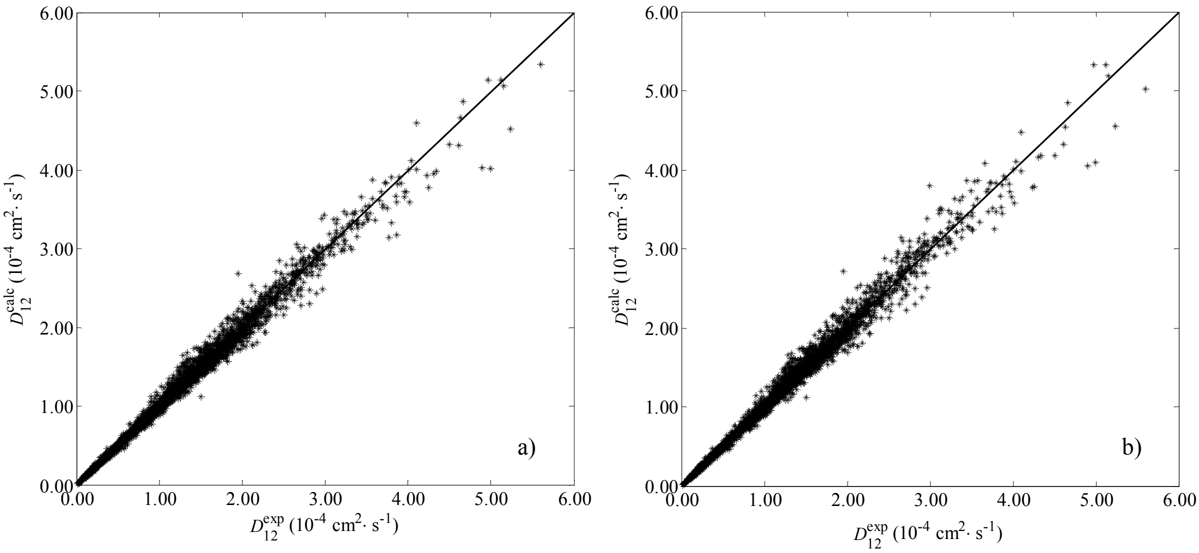

Figure 1. Calculated *versus* experimental tracer diffusivities for two correlations testes in this work: a) Eq. (4); b) Eq. (9).

seven equations, thus they have been compiled in Supplementary Material of the original paper as Figures S1 to S7. From these representations it is possible to confirm the good distribution of points along diagonals, which emphasizes their unbiased behaviour. Together with the low AARDs found, they prove their reliability and desirable statistical behaviour.

The prediction capability of the 2-parameter correlations listed in Table 2 was tested according to the following procedure: *i*) firstly, the mean experimental diffusivity, $\overline{D}_{12}^{\mathrm{Exp}}$, of each binary system was computed; *ii*) secondly, the corresponding standard deviation, σ, was calculated; *iii*) then, the diffusivities closest to $\overline{D}_{12}^{\mathrm{Exp}}-\sigma$ and $\overline{D}_{12}^{\mathrm{Exp}}+\sigma$ were selected from each set of data; *iv*) subsequently, the parameters a_i and b_i were calculated using these two diffusion coefficients, *i.e.* they were taken as the roots of equation i for each system; in the whole, the number of experimental data utilized was twice the number of systems, *i.e.* $2\times 539=1078$; *v*) The diffusivities for the remaining conditions of database were estimated by all correlations using such parameters; the number of points here was $8219-1078=7141$; the AARDs were computed for each correlation and solvent-solute pair, and the global AARDs were calculated for each correlation. In Table 3 the prediction results thus obtained are also listed for discussion. As can be observed, only slight increments in the global deviations were found passing from correlation to prediction: 3.23% *versus* 4.46% with Eq. (1), 3.05% *versus* 4.41%

with Eq.(2), etc. These results elucidate the fine predictive capability of all correlations studied, particularly Eqs. (1) - (4) and (9). It is remarkable that only two experimental values are sufficient to get good parameters (a_i and b_i) for the subsequent estimation of reliable diffusivities far away from the conditions of the experimental data utilized to fit them.

Before finishing, the models behaviour may be further evidenced by plotting the experimental and calculated tracer diffusion coefficients of very distinct systems in terms of solutes and/or solvents like, for instance, benzoic acid in water, oxygen in water, 1,3-divinylbenzene in carbon dioxide, and 2-butanone in carbon dioxide against solvent viscosity (Figures 2.a and 2.c) or solvent density (Figures 2.b and 2.d). In Figures 2.a and 2.b the results reached by all models are graphed, while in Figures 2.c and 2.d only the diffusivities calculated by Eqs. (4) and (9) are represented. As expected in advance, the selected models perform similarly and correlate accurately the experimental data: AARD (benzoic acid in water between 2.09 and 3.53%, oxygen in water between 1.49 and 5.90%, 1,3-divinylbenzene in CO_2 between 1.34 and 1.55%, and 2-butanone in CO_2 between 1.72 and 1.78%). In addition, the plots of Figures 2.c and 2.d point out the fine representation achieved by Eqs. (4) and (9) for distinct isotherms.

4.PVII.6. Conclusions

In this work nine correlations are proposed and/or analysed for the estimation of tracer diffusion coefficients of liquid and supercritical systems composed of polar/non-polar, symmetrical/asymmetrical, small/large, and light/heavy molecules. They are very simple, involve only two parameters, and proved to be very accurate over wide ranges of temperature and density (average deviations between 2.78% and 4.44%). A very stringent test was implemented with success to test their prediction ability. In the whole, Eqs. (2) – – (4) and (9) can be selected due to their excellent behaviour, for which the average absolute relative deviations range from 2.78% to 3.05% (correlation) and 4.21% to 4.44% (prediction).

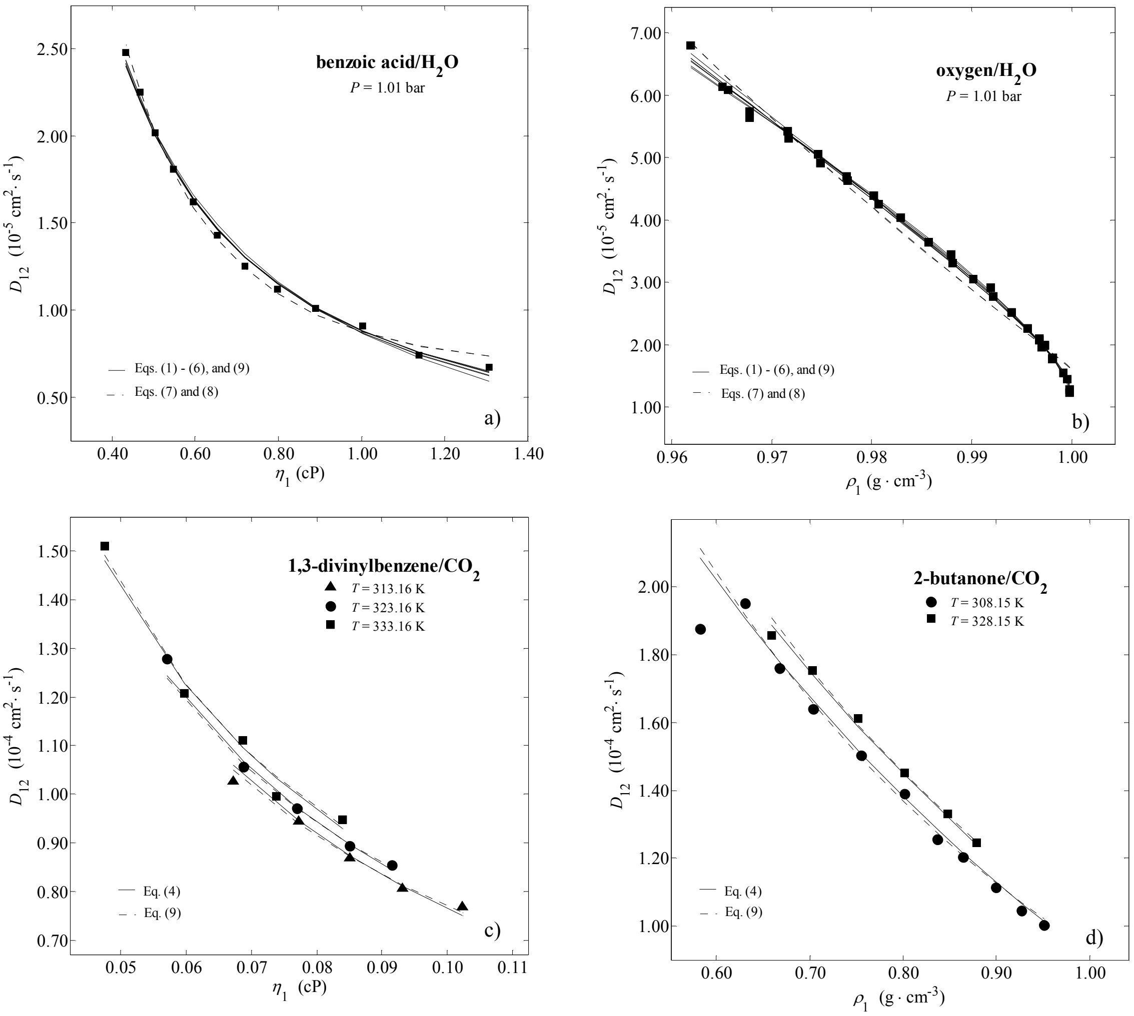

Figure 2. Experimental and calculated tracer diffusion coefficients for constant temperatures or pressures: a) benzoic acid in water; b) oxygen in water; c) 1,3-divinylbenzene in carbon dioxide; d) 2-butanone in carbon dioxide.

Nomenclature

AARD	Average absolute relative deviation
a_i, b_i	Fitting parameters of equation i in Table 1
B	Constant characteristic of the solvent-solute pair in Dymond equation
C	Constant characteristic of the solvent-solute pair in Grushka *et al.* equation
D_{12}	Tracer diffusion coefficient
k_{B}	Boltzmann constant
M	Molecular weight
M_{12}	Reduced molar mass of the system
NDP	Number of data points
NS	Number of systems
P_{c}	Critical pressure
$\Re_{\mathrm{g}}$	Universal gas constant
T	Absolute temperature
T_{c}	Critical temperature
T_{bp}	Normal boiling point
TLSM $_{\mathrm{d}}$	Tracer diffusion coefficient model due to Liu, Silva and Macedo
V	Molar volume
V_{c}	Molar critical volume
V_{D}	Constant related primarily with the solvent in Dymond equation
V_{bp}	Molar volume at normal boiling point

Greek letters

$\varepsilon_{\mathrm{LJ},i}$	LJ parameter of component $i = 1, 2$ or mixture $i = 12$
ϕ_1	Dimensionless association factor in Wilke-Chang equation
η_1	Solvent viscosity
ρ_1	Solvent density
ρ_{D}	Parameter in Grushka *et al.* equation
$\rho_{\mathrm{r},1}$	Reduced density of the solvent using critical density
σ_i	Diameter of component $i = 1, 2$ or mixture $i = 12$
$\sigma_{\mathrm{LJ},i}$	LJ parameter of component $i = 1, 2$ or mixture $i = 12$

Subscripts

1	Solvent
2	Solute
12	Binary
eff	Refers to effective hard sphere diameter
LJ	Lennard-Jones

Superscripts

*	Reduced quantity
calc	Calculated value
exp	Experimental value

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Paper VIII

Adapted from

Accurate Hydrodynamic Models for the Prediction of Tracer Diffusivities in Supercritical Carbon Dioxide

Journal of Supercritical Fluids, **2013**, 83, 15–27.

Abstract

The tracer diffusion coefficients, D_{12}, are fundamental properties for the design and simulation of rate-controlled processes. Nowadays, under the scope of the biorefinery concept and strict environmental legislation, the D_{12} values are increasingly necessary for extractions, reactions, and chromatographic separations carried out at supercritical conditions, particularly using carbon dioxide. Hence, the main objective of this work is the development of accurate and simple models for the pure prediction of D_{12} values in supercritical CO_2. Two modified Stokes-Einstein equations (mSE_1 and mSE_2) are proposed and validated using a large database comprehending extremely distinct molecules in terms of size, molecular weight, polarity and sphericity. The global deviations achieved by the mSE_1 (Eqs. (2) + (13) and mSE_2 (Eqs. (5) + (13) + (3) + (4)) models are only 6.38% and 6.75%, respectively, in contrast to the significant errors provided by well-known predictive correlations available in the literature: Wilke-Chang, 12.17%; Tyn-Calus, 17.01%; Scheibel, 19.04%; Lusis-Ratcliff, 27.32%; Reddy-Doraiswamy, 79.34%; Lai-Tan, 25.82%. Furthermore, the minimum and maximum deviations achieved by the new models are much smaller than those of the reference equations adopted for comparison. In conclusion, our mSE_1 and mSE_2 models can be recommended for the prediction of tracer diffusivities in supercritical CO_2.

4.PVIII.1. Introduction

The binary diffusion coefficient, D_{12}, has a great importance in the design and simulation of rate controlled separations and multiphase reactions, in order to compute the convective mass transfer coefficients from dimensionless correlations [1] and/or the catalysts efficiency factors [2].

The supercritical fluid extraction (SFE) is one field of rapid technological development nowadays since it combines characteristics of conventional solvent extraction and distillation with the unique features of supercritical fluids (SCF): liquid-like densities, gas-like viscosities, diffusivities between those of gases and liquids, and the ability to tune such properties near the critical point by small changes of temperature and/or pressure, or by introducing small quantities of polar co-solvents [3-4]. More recently, the SCFs are finding large interest as solvents/desorbents in preparative chromatography and Simulated Moving Bed (SMB) separations [5-6]. When used as mobile phase in these processes, high separation efficiency, reduced pressure drop, and reduced eluent consumption may be achieved [5-8]. Some examples that evidence good results accomplished by supercritical SMB are separation of 1-phenyl-1-propanol enantiomers [9], bi-naphthol enantiomers and phytol isomers [10], ethyl linoleate and ethyl oleate [11].

With respect to the binary diffusion coefficients measured and published in the literature, it is clear they reflect their practical interest in terms of final applications. For instance, fatty acids, triacylglycerides, amino acids, sugars, triterpenoids, and phenolic compounds have significant relevance in food, pharmaceutical, and fuel industries [12-19]. Hence, their presence in natural resources and biomass residues, along with the possibility to extract them with pure and modified supercritical carbon dioxide (SC-CO_2) instead of organic solvents, increasingly requires their diffusivities [1, 4]. Also worth mentioning are organometallic solutes in SC-CO_2, like palladium(II) acetylacetonate and cobalt(III) acetylacetonate, which have been largely used in the preparation and processing of advanced functional materials, as catalysts or precursors [20-21]. Therefore, the existence of D_{12} values in SC-CO_2 is crucial for the simulation and design of these processes, which requires the development of accurate models for their estimation since it is impossible to carry out experimental measurements for all systems at all operating conditions.

Several approaches for the calculation of diffusion coefficients in dense fluids are available in the literature, such as the landmark Enskog theory [22-24] for the hard sphere fluid and its modifications for real systems [22, 24], the effective hard sphere diameter method [24-27], the free-volume theories [24, 28-30], the van der Waals [24, 31-32] and rough hard sphere principles [24, 33-39], the hydrodynamic models based on the Stokes-Einstein equation [3, 40], the Eyring activated-state theory [41], and excess entropy scaling laws [24, 42-44]. Most of these models and approaches were described and reviewed by Reid *et al*. [40], Liong *et al*. [3], Silva and Liu [24], and Medina [45].

In order to address the limitations of most models found in the literature, we recently developed accurate D_{12} expressions validated with large databases and applicable to wide ranges of temperature and pressure. A brief description of these approaches is provided in the following.

A molecularly based model for real systems [46] was derived from an accurate hard sphere expression, where the softness of the repulsive interactions and the contribution of attractive forces were embodied by means of the effective hard sphere diameter method and by coupling an attractive exponential term, respectively. With just one parameter, it arises an average absolute relative deviation (AARD) of 4.40% for 314 binary systems and 5421 data points including gas, liquid and supercritical fluids. A distinct expression [47] was devised according to the Rice and Gray approach. It involves one parameter and achieves an AARD = 4.26% for 309 systems and 5341 data points, interpreting equally well the diffusive phenomena in gases, liquids and SCFs.

These two previous equations should only be applied to non-polar or weakly polar binaries. Hence a more general model [48] was developed later for the diffusivities of systems containing at least one polar component (solute and/or solvent). This is a sensitive case for which the existent equations usually fail, particularly when hydrogen-bonding solvents are involved. The new model includes friction coefficients in the Rice and Gray seminal equation to take into account a repulsive hard sphere core, a soft Lennard-Jones contribution, and specific polar interactions. With two parameters, it provides only 3.65% of error for 211 polar systems and 3463 data points, and 4.27% for systems with strictly polar solvents (141 systems and 1994 experimental points).

A hybrid free-volume equation [49], where repulsive and attractive interactions were taken into account by the concepts of free volume and activation energy, respectively, was presented later for supercritical CO_2 and liquid water due to the large importance of both solvents in research and industry. The model embodies one parameter that is system specific, and achieves an AARD = 3.56% for 289 systems and 5485 data points.

More recently, an universal equation [50] based on the Lennard-Jones (LJ) model was published for accurate calculation of D_{12} values for polar, weakly polar, and non-polar solutes and/or solvents, applicable in gas, liquid and supercritical states. It requires two parameters – the molecular diameter of the solvent and a diffusion activation energy – and reaches AARDs = 2.65% and 2.97% for polar (180 systems/2335 points) and non-polar or weakly polar (307 systems/5958 points) mixtures, respectively, totalizing 487 systems with 8293 points. With regard to the individual physical states of the systems, the average deviations are 1.56% for gaseous (73 systems/1036 points), 2.90% for supercritical (173 systems/4398 points), and 2.92% for liquid (241 systems/2859 points).

In the whole, the good results accomplished by the previous models are due to their molecular fundamentals and solid physical principles. It is worth noting their excellent extrapolation ability. However, they are frequently lengthy for calculations, which may be an obstacle for readers out of this research area or from industry. Hence, spreadsheets for D_{12} calculation are provided online in the supplemental material of the original papers. With the objective to make available very simple and accurate equations for D_{12}, empirical and semi-empirical models [51] dependent only on temperature and/or solvent density and/or solvent viscosity were later published. They involve two parameters and reach global AARDs between 2.78% (when D_{12} is correlated with temperature and solvent viscosity) and 4.44% (D_{12} depends only upon solvent viscosity) for 539 binary systems and 8219 data points in liquid and supercritical fluids. These equations exhibit very good extrapolation ability also.

A common feature of these models is that they require one or two parameters that must be previously fitted to experimental diffusivities. Nonetheless, it is fundamental to possess accurate expressions for their pure prediction. With this respect, hydrodynamic equations are good alternatives, since they are simple, involve a small set of input data, and are frequently predictive. One may cite the Wilke-Chang [52], Tyn-Calus [53], Hayduk-Minhas [54], Reddy-Doraiswamy [55], Scheibel [56], and Lusis-Ratcliff [57] equations. However, significant errors can be obtained, in particular when they are applied over large ranges of temperature and density, or near the critical point. Magalhães *et al*. [49, 51] and Lito *et al*. [50] found systematically average errors between 20% and 60% when extensive databases are used to test them.

In this work two modified Stokes-Einstein equations are proposed for the pure prediction of D_{12} values of solutes in supercritical CO_2. The validation involved the largest database compiled for this purpose. A comparison with a significant number of predictive equations is also accomplished.

4.PVIII.2. New Hydrodynamic Models for D_{12}

The hydrodynamic approach to mass transport is based on the Stokes-Einstein expression which establishes that diffusivities are directly proportional to the absolute temperature, T, and inversely proportional to the solvent viscosity, η_1:

$$D_{12} = \frac{k_B T}{6 \pi r_2 \eta_1} \tag{1}$$

Here k_B is the Boltzmann's constant, r_2 is the radius of the solute molecule, and subscripts 1 and 2 denote solvent and solute, respectively. The Stokes-Einstein model was firstly derived assuming that a large rigid spherical molecule of solute is moving through a continuum of solvent ($r_1 << r_2$) under infinitely dilute conditions [40, 58].

A large group of hydrodynamic equations like those mentioned in the Introduction, was originally developed for liquids and then extended to SCFs [3, 59], giving rise to significant overestimations of D_{12}, most likely due to their inability to describe the role of viscosity in the diffusion process [3, 60-61]. Since the Stokes-Einstein assumptions do not hold for all conditions, namely for SCF systems, some modifications like power laws relationships of the type $D_{12} \propto \eta_1^{-\alpha}$ $(\alpha > 0)$ have been suggested [3, 61-62]. In this work this approach is also adopted.

Some authors [54] also realized the need for a more specific correlation depending on the type of solute-solvent system. Since the effect of solvent viscosity on the rate of diffusion also depends on the size of diffusing molecules, the solute molar volume should also be introduced, being evaluated at the normal boiling point ($V_{\mathrm{bp},2}$). In addition, the diffusivities in SCFs get values between those of liquids and gases, which means that an additional dependence on the molecular weight of the solute (M_2) should be taken into account, as suggested by the kinetic theory of gases [22, 30]. Consequently, the following relationship is embodied in this work: $D_{12} \propto (M_2 V_{\mathrm{bp},2})^{-\beta}$ $(0 < \beta < 1)$.

Finally, after softening the temperature influence of the Stokes-Einstein equation ($D_{12} \propto (T/\eta_1)^{\alpha}$ with $\alpha > 0$), the resulting model proposed in this work is:

$$D_{12} = A'\left(\frac{T}{\eta_1}\right)^{\alpha'} \frac{1}{(M_2 V_{\mathrm{bp},2})^{\beta'}} \tag{2}$$

This equation will be henceforth called *modified Stokes-Einstein*-1 or mSE$_1$. It involves exponents α' and β', and the frontal coefficient A' that will be fitted to the whole database compiled. The units chosen for the variables of Eq. (2) are $\mathrm{cm^2 \cdot s^{-1}}$, K, cP, $\mathrm{g \cdot mol^{-1}}$, and $\mathrm{cm^3 \cdot mol^{-1}}$.

An alternative correlation for D_{12} in SC-CO$_2$ can be obtained assuming similar dependencies on the temperature, solute molecular weight, and solvent viscosity, but including the influence of the solute surface tension at normal boiling point ($\sigma_{\mathrm{bp},2}$) *via* its parachor ($\mathbf{P}_{\mathrm{bp},2}$). The relation between both variables is $\mathbf{P}_{\mathrm{bp},2} = V_{\mathrm{bp},2}\,\sigma_{\mathrm{bp},2}^{1/4}$ [40]. For simplicity, and $\sigma_{\mathrm{bp},2}$ is estimated in this work by the Brock and Bird corresponding states method [40, 63] combined with Miller's equation [40, 64]:

$$\sigma_{\mathrm{bp},2}\left(\mathrm{g \cdot cm^{-2}}\right) = P_{\mathrm{c},2}^{2/3}\, T_{\mathrm{c},2}^{1/3} \left(0.132\,\alpha_{\mathrm{c},2} - 0.279\right)\left(1 - T_{\mathrm{bp},2,\mathrm{r}}\right)^{11/9} \tag{3}$$

$$\alpha_{\mathrm{c},2} = 0.9076\left[1 + \frac{T_{\mathrm{bp},2,\mathrm{r}} \ln\left(P_{\mathrm{c},2}/1.013\right)}{1 - T_{\mathrm{bp},2,\mathrm{r}}}\right] \tag{4}$$

where $P_{\mathrm{c},2}$ (bar), $T_{\mathrm{c},2}$ (K) and $T_{\mathrm{bp},2,\mathrm{r}} = T_{\mathrm{bp},2}/T_{\mathrm{c},2}$ are the critical pressure, the critical temperature, and the reduced normal boiling point of solute, respectively.

The final expression proposed in this essay for D_{12} contains three parameters (α'', β'', A'') that will be fitted to the whole database, being hereafter identified by *modified Stokes-Einstein*-2 or mSE$_2$:

$$D_{12} = A''\left(\frac{T}{\eta_1}\right)^{\alpha''} \frac{1}{\left(M_2\,\mathbf{P}_{\mathrm{bp},2}\right)^{\beta''}} \qquad \text{and} \qquad \mathbf{P}_{\mathrm{bp},2} = V_{\mathrm{bp},2}\,\sigma_{\mathrm{bp},2}^{1/4} \tag{5}$$

The units chosen for the previous variables are $\mathrm{cm^2 \cdot s^{-1}}$, K, cP, $\mathrm{g \cdot mol^{-1}}$, $\mathrm{cm^3 \cdot g^{1/4} \cdot s^{-1/2} \cdot mol^{-1}}$, $\mathrm{cm^3 \cdot mol^{-1}}$, and $\mathrm{g \cdot cm^{-3}}$.

Before concluding this section, it is important to refer that experimental solute molar volumes at normal boiling point, $V_{\mathrm{bp},2}$, are frequently unavailable, which requires their estimation by group contribution methods or others. The well-known method of Tyn-Calus [40, 65] is frequently used for this purpose and will be selected in this work due to its simplicity. However, their deviations to the experimental values need to be previously corrected. This is the first task of Section 4.PVIII.5 (Results and Discussion).

4.PVIII.3. Models Adopted for Comparison

The equations proposed in this work are purely predictive since their parameters will be fitted to the global database, thus acquiring an universal character. Accordingly, only predictive models were adopted for comparison, namely: Wilke-Chang (WC) [52], Tyn--Calus (TC) [53], Scheibel (Sch) [56], Lusis-Ratcliff (LR) [57], Reddy-Doraiswamy (RD) [55], and Lai-Tan (LT) [66]. In the following, their expressions are briefly presented.

4.PVIII.3.1. Wilke-Chang equation [52]

In this equation, ϕ_1 is a dimensionless association factor of the solvent, η_1 is the solvent viscosity (cP), M_1 is the solvent molecular weight ($\mathrm{g \cdot mol^{-1}}$), $V_{\mathrm{bp},2}$ is solute molar volume at its normal boiling point ($\mathrm{cm^3 \cdot mol^{-1}}$).

$$D_{12,\mathrm{WC}}\left(\mathrm{cm^2 \cdot s^{-1}}\right) = 7.4 \times 10^{-8} \frac{T\sqrt{\phi_1 M_1}}{\eta_1 V_{\mathrm{bp},2}^{0.6}} \tag{6}$$

4.PVIII.3.2. Tyn-Calus equation [53]

In this equation $\mathbf{P}_i$ identifies the parachor of component *i*, which is related with the liquid surface tension and may be estimated by additive group contributions. For most organic solvents, an approximation is used in the calculation. The precise and approximate correlations, in the same units of the Wilke-Chang model, are given by, respectively:

$$D_{12,\mathrm{TC}}\left(\mathrm{cm^2 \cdot s^{-1}}\right) = 8.93 \times 10^{-8} \left(\frac{V_{\mathrm{bp},2}}{V_{\mathrm{bp},1}^2}\right)^{1/6} \left(\frac{\mathbf{P_1}}{\mathbf{P_2}}\right)^{0.6} \frac{T}{\eta_1} \tag{7}$$

$$D_{12,\mathrm{TC}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=8.93\times10^{-8}\frac{V_{\mathrm{bp},1}^{0.267}}{V_{\mathrm{bp},2}^{0.433}}\frac{T}{\eta_1} \qquad (8)$$

where $V_{\mathrm{bp},1}$ is the solvent molar volume at its normal boiling point ($\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$).

4.PVIII.3.3. ***Scheibel equation*** [56]

Here the units are those of the Wilke-Chang correlation.

$$D_{12,\mathrm{Sch}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{8.2\times10^{-8}T}{\eta_1 V_{\mathrm{bp},2}^{1/3}}\left[1+\left(\frac{3V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)^{2/3}\right] \qquad (9)$$

4.PVIII.3.4. ***Lusis-Ratcliff equation*** [57].

Here the units are those of the Wilke-Chang correlation.

$$D_{12,\mathrm{LR}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\frac{8.52\times10^{-8}T}{\eta_1 V_{\mathrm{bp},1}^{1/3}}\left[1.40\left(\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)^{1/3}+\left(\frac{V_{\mathrm{bp},1}}{V_{\mathrm{bp},2}}\right)\right] \qquad (10)$$

4.PVIII.3.5. ***Reddy-Doraiswamy equation*** [55]

$$\begin{gathered}D_{12,\mathrm{RD}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=\beta\times\frac{T\sqrt{M_1}}{\eta_1\left(V_{\mathrm{bp},1}V_{\mathrm{bp},2}\right)^{1/3}}\\ V_{\mathrm{bp},1}/V_{\mathrm{bp},2}\le1.5\ \Rightarrow\ \beta=10\times10^{-8}\\ V_{\mathrm{bp},1}/V_{\mathrm{bp},2}>1.5\ \Rightarrow\ \beta=8.5\times10^{-8}\end{gathered} \qquad (11)$$

4.PVIII.3.6. ***Lai-Tan equation*** [66]

This equation has been only validated for supercritical carbon dioxide systems. $V_{c,2}$ is the critical volume of the solute, in $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$. The remaining units are those of the Wilke-Chang model.

$$D_{12,\mathrm{LT}}\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)=2.50\times10^{-7}\frac{T\sqrt{M_1}}{\left(10\times\eta_1\right)^{0.688}V_{c,2}^{1/3}} \qquad (12)$$

4.PVIII.4. Database and Data for the Calculations

A large database of experimental tracer diffusivities in SC-CO_2 was compiled to validate the new hydrodynamic models: 156 systems totalizing 4425 data points. A detailed description of the systems may be consulted in Table S.1 (Supplementary Data), namely their identification, number of points, reduced ranges of temperature, pressure and solvent density, and data sources. Data available exclusively in graphical form was not included in the calculations.

The name, molecular formula, CAS number, molecular weight, critical constants, normal boiling point, and molar volume at normal boiling point of all molecules involved in calculations are listed in Table S.2 (Supplementary Data). Regarding solvent (SC-CO_2) densities, they were computed by the correlation of Pitzer and Schreiber [67] when they were not provided by the authors of the data used. The viscosities of SC-CO_2 were estimated by the correlation of Altunin and Sakhabetdinov [68] whenever absent in the original papers. The solute molar volumes at normal boiling point were estimated by Tyn-Calus equation [40, 69]. The non-existent critical constants were estimated by Joback [40, 70-71], Somayajulu [72], Klincewicz [40, 73], Ambrose [40, 74-75], Wen-Qiang [76], and Constantinou-Gani [77] methods.

4.PVIII.5. Results and Discussion

The results achieved with the modified Stokes-Einstein equations (mSE$_1$ and mSE$_2$) proposed in this work are presented and analysed in this section, along with the comparative results of the predictive hydrodynamic equations previously selected for comparison. The necessary relation given between experimental and calculated $V_{\mathrm{bp},2}$ will be firstly obtained since is necessary in all calculations.

The new mSE$_1$ and mSE$_2$ models require the molar volume at normal boiling point of the solute, which is frequently non-available. In such cases, estimated values have to be utilized. However, there is a systematic deviation between experimental and predicted $V_{\mathrm{bp},2}$, which demands a different and rational approach. Hence, one starts by plotting $V_{\mathrm{bp},2}^{\mathrm{exp}}$ *versus* $V_{\mathrm{bp},2}^{\mathrm{TC}}$ in order to disclose an explicit regression between both; the superscript TC means that $V_{\mathrm{bp},2}$ is computed by Tyn-Calus method [40, 65]. This plot is illustrated in

Figure 1 for 97 solute molecules being possible to observe a clear trend that is well represented by:

$$V_{\mathrm{bp},2}^{\exp} = 1.459\left(V_{\mathrm{bp},2}^{\mathrm{TC}}\right)^{0.894} \tag{13}$$

Based on this figure, it is worth noting the large discrepancies that would be expected if estimated values were substituted directly in D_{12} models whenever experimental data were absent. Accordingly, Eq. (13) will be henceforth substituted in Eqs. (2) and (5), which means that only estimated solute molar volumes at normal boiling point will be utilized in calculations for consistency and rigor.

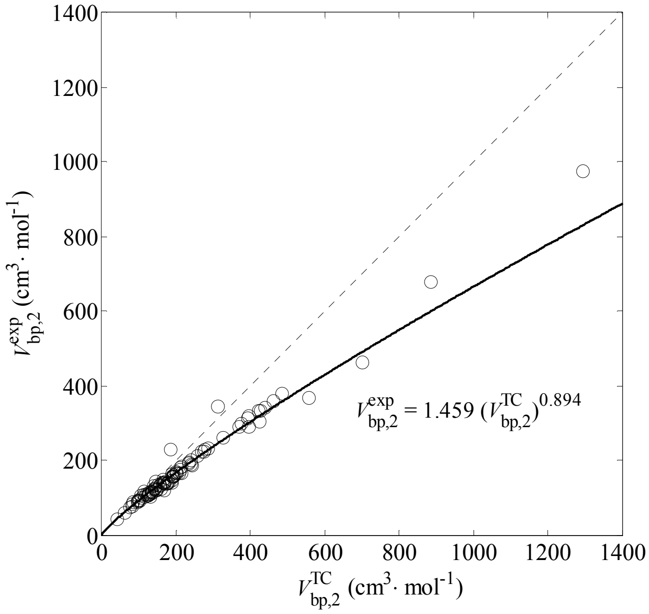

Figure 1. Relationship between experimental and calculated molar volumes at normal boiling point (by Tyn-Calus method [40, 69]).

The parameters of the new models – Eqs. (2) and (5) combined with Eq. (13) – – were fitted to the experimental diffusivities of database (Section 4.PVIII.4), but specific constants were additionally optimized for *n*-alkanes since most equations generally fail to describe this group of molecules [51, 78-79]. The resulting parameters are compiled in Table 1. It is interesting to observe that similar constants arose for both mSE_1 and mSE_2 models. Nonetheless, significantly different values appeared when *n*-alkanes were treated in separate: A' and A'' decayed three orders of magnitude, α' and α'' doubled their values, while β' and β'' dropped by half. Let us now inspect Eq. (2) (similar treatment can be accomplished with Eq. (5)). The dependence of $\ln D_{12}$ upon $\ln(T/\eta_1)$ and $\ln(M_2 V_{\mathrm{bp},2}^{\mathrm{TC}})$ is linear, *i.e.* $\ln D_{12}$ is a plane in these coordinates. However, Table 1 shows that for *n*-alkanes this dependence is stronger in $\ln(T/\eta_1)$ and weaker in $\ln(M_2 V_{\mathrm{bp},2}^{\mathrm{TC}})$, and a notorious shift of their zero intercepts emerge. This is consistent with other authors' findings, since the D_{12} values of *n*-alkanes were frequently overestimated by the hydrodynamic correlations. For this reason, dedicated constants are proposed for the particular case of these solutes, similarly to previous works [80-81].

The detailed results obtained, together with other relevant information, are shown in Table 2, namely the identification of the systems, the corresponding data sources, number of data points (NDP), and average absolute relative deviations (AARDs) achieved by our models and by the equations adopted for comparison. The AARD was computed as:

Table 1. Optimized parameters (universal constants) of the new D_{12} equations proposed in this work.

Model	Eqs.	A' or A''	α' or α''	β' or β''
mSE1	(2) + (13)	1.1335×10^{-6}	0.8468	0.2634
mSE2	(5) + (13) + (3) – (4)	1.8186×10^{-6}	0.8445	0.2898
mSE1 for *n*-alkanes	(2) + (13)	2.7845×10^{-9}	1.4311	0.1239
mSE2 for *n*-alkanes	(5) + (13) + (3) – (4)	3.2544×10^{-9}	1.4311	0.1316

$\mathrm{mSE_1}$ = New *modified Stokes-Einstein*-1 model; $\mathrm{mSE_2}$ = New *modified Stokes-Einstein*-2 model.

$$\mathrm{AARD}(\%) = \frac{100}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left| \frac{D_{12}^{\mathrm{calc}} - D_{12}^{\mathrm{exp}}}{D_{12}^{\mathrm{exp}}} \right|_i \tag{14}$$

Table 2 shows that small deviations were obtained in general, and evidences that the errors for *n*-alkanes were substantially diminished in comparison to other equations.

Table 2. Calculated results (AARDs) for the tracer diffusivities of solutes in supercritical CO_2 achieved by the new models (mSE_1 and mSE_2) and by the expressions adopted for comparison.

		New models†		Models from the literature†					
		mSE_1	mSE_2	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
acetone	214	3.78	3.45	7.01	5.07	24.16	15.39	40.49	10.38
acridine	6	4.14	2.99	4.93	12.06	10.72	20.98	72.93	27.22
allylbenzene	15	4.88	4.63	5.36	8.42	11.96	17.71	62.71	16.33
aniline	15	26.17	23.74	42.40	40.42	63.36	57.38	99.56	33.65
anisole	15	6.03	4.90	17.53	19.34	33.27	32.11	72.58	16.31
anthracene	22	8.20	10.22	1.86	9.02	9.95	17.80	65.73	14.67
arachidonic acid (AA)	75	4.80	4.50	9.70	16.13	7.12	25.84	92.80	41.11
AA ethyl ester	48	3.46	3.33	15.16	10.26	0.94	19.76	84.76	30.43
behenic acid ethyl ester	17	5.54	4.57	21.34	5.03	6.43	14.66	78.86	31.30
benzene	249	8.92	8.86	8.70	8.54	18.73	14.22	43.82	9.34
benzoic acid	35	6.50	6.05	10.18	14.17	22.93	25.05	67.59	15.57
benzyl acetate	15	8.49	7.12	19.98	27.43	34.52	39.09	89.31	28.09
benzylacetone	15	11.40	9.75	6.19	17.90	18.07	27.48	80.40	30.46
biphenyl	24	6.40	8.66	10.13	6.94	6.96	10.78	56.82	10.04
2-bromoanisole	15	3.90	2.83	16.52	23.81	30.64	35.12	83.97	30.69
bromobenzene	21	8.06	9.84	13.90	15.01	29.41	27.59	65.77	11.96
2-butanone	40	3.59	2.78	4.23	3.92	18.04	13.42	43.41	4.71
n-butylbenzene	15	2.48	2.24	6.41	14.76	19.07	24.81	72.04	16.57
tert-butylbenzene	15	3.51	3.60	3.81	11.41	15.73	21.20	66.91	14.03

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE_1	mSE_2	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
butyric acid ethyl ester	16	3.68	3.59	3.79	8.82	16.54	19.16	60.49	6.58
caffeine	25	10.32	8.75	19.34	31.71	32.43	42.21	100.59	28.47
capric acid ethyl ester	16	4.42	4.05	2.21	13.00	9.90	21.83	76.25	16.75
caprylic acid ethyl ester	16	3.70	3.53	1.67	12.94	12.42	22.03	73.46	14.33
β-carotene	90	7.14	8.24	14.88	20.36	5.82	33.25	112.10	66.19
L-carvone	27	5.88	5.44	3.66	12.00	12.01	21.08	71.52	24.41
chlorobenzene	21	3.43	3.80	12.70	13.20	28.30	25.85	62.65	10.58
chrysene	4	9.49	11.70	16.16	2.80	5.59	6.63	56.60	18.17
citral	15	3.88	3.91	8.63	5.29	3.45	13.20	63.44	11.19
cobalt(III) acetylacetonate	38	2.05	26.40	11.53	29.97	25.24	40.06	104.07	47.22
copper(II) trifluoroacetylacetonate	12	6.21	6.53	37.09	49.65	53.26	62.37	125.99	52.90
dibenzo-24-crown-8	28	2.30	5.73	12.73	13.08	2.71	22.77	89.14	51.41
15-crown-5	29	7.45	9.32	7.85	12.64	11.20	21.59	74.02	15.09
cycloheptanone	8	11.76	11.49	24.01	26.38	40.45	39.72	83.17	18.83
cyclononanone	8	9.79	9.28	17.62	25.13	31.85	36.52	86.08	22.69
cyclopentanone	8	10.67	8.62	25.81	23.48	44.65	38.71	75.00	9.61
n-decane	5	2.85	2.94	31.63	23.46	23.58	17.27	17.33	21.11
dibenzyl ether	15	10.03	8.18	18.77	32.36	32.74	43.15	102.35	38.16
1,2-dichlorobenzene	15	2.52	3.05	18.56	21.07	34.19	33.75	75.69	17.55
1,3-dichlorobenzene	4	4.28	3.12	21.73	24.59	37.67	37.52	81.05	23.87

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE_1	mSE_2	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
p-dichlorobenzene	13	3.57	3.38	10.61	16.00	24.31	27.05	71.04	17.02
diethyl ether	17	5.50	6.55	10.51	10.94	23.20	21.31	57.38	8.14
1,2-diethylbenzene	15	2.94	2.76	8.78	16.90	21.78	27.24	74.88	17.28
1,4-diethylbenzene	15	3.52	3.42	7.81	16.25	20.64	26.44	74.26	18.05
diisopropyl ether	15	8.40	7.22	6.63	7.07	11.10	14.04	54.30	11.51
2,3-dimethylaniline	15	18.80	17.19	16.04	24.54	29.92	35.59	86.17	33.42
2,6-dimethylaniline	15	14.08	11.47	11.47	19.64	24.80	30.25	78.84	28.06
1,1′-dimethylferrocene	68	5.01	5.01	12.16	20.35	25.53	31.02	79.91	18.70
2,6-dimethylnaphthalene	6	4.34	4.23	7.15	9.26	8.88	17.98	67.76	18.68
2,7-dimethylnaphthalene	6	4.44	4.36	6.91	6.00	5.64	13.01	60.69	16.04
2,4-dimethylphenol	15	10.62	7.78	23.84	27.82	39.73	40.68	86.67	24.55
diolein	9	5.51	5.75	10.37	23.45	8.90	35.72	114.15	48.58
1,3-divinylbenzene	15	2.57	2.16	9.61	16.12	22.96	26.82	72.23	16.58
docosahexaenoic acid (DHA)	63	7.62	6.99	7.28	19.86	8.29	30.05	100.02	48.35
DHA ethyl ester	65	4.21	4.07	16.73	9.27	2.00	18.88	84.14	31.39
DHA methyl ester	17	3.83	3.82	16.76	8.37	2.47	17.74	81.78	32.12
n-dodecane	5	3.25	3.24	33.43	23.52	25.41	17.53	19.06	19.59
eicosapentaenoic acid (EPA)	55	5.37	4.66	7.79	17.55	7.30	27.28	94.51	41.67
EPA ethyl ester	48	3.79	3.77	14.98	10.14	1.02	19.58	84.21	29.92
EPA methyl ester	17	3.63	3.66	17.37	7.27	3.34	16.49	79.62	30.48

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE$_1$	mSE$_2$	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
ethanol	24	3.86	4.23	13.85	5.82	36.63	22.04	41.64	9.68
ethyl acetate	16	9.14	9.28	21.86	21.70	38.05	34.61	72.88	7.05
ethylbenzene	15	3.72	3.77	3.06	5.26	14.43	15.59	53.87	4.84
ethyl benzoate	15	7.69	8.12	18.87	26.42	33.25	37.94	87.96	24.86
2-ethyltoluene	15	3.04	3.02	7.18	12.90	20.18	23.45	67.01	10.53
3-ethyltoluene	15	3.39	3.26	6.47	12.47	19.26	22.88	66.70	9.09
4-ethyltoluene	15	2.04	2.22	8.22	14.59	21.41	25.17	69.91	12.72
eugenol	15	15.48	12.94	17.29	28.35	31.11	39.19	94.09	39.69
ferrocene	107	4.84	5.63	17.43	21.04	32.55	33.28	76.62	17.31
2-fluoroanisole	15	11.07	10.25	18.48	22.85	33.51	35.01	79.91	26.66
fluorobenzene	15	4.25	4.13	15.22	14.17	31.91	27.68	62.72	10.83
3-fluorophenol	4	12.21	8.68	13.15	17.99	27.33	29.44	73.37	24.26
geraniol	4	14.94	13.74	3.34	18.04	15.70	27.33	83.12	35.80
n-heptane	5	1.13	1.25	23.89	18.78	14.72	11.45	21.00	18.71
hexachlorobenzene	14	14.14	16.62	10.99	13.01	12.63	20.34	71.35	14.18
1-hexadecene	11	8.90	8.82	10.30	21.80	16.19	29.84	91.99	21.13
1,1,1,5,5,5-hexafluoroacetylacetone	15	5.29	4.94	18.95	27.98	33.14	39.26	91.59	32.24
n-hexane	5	2.29	2.25	19.88	16.10	9.93	8.07	23.60	16.44
iodobenzene	20	7.61	10.30	20.62	22.99	36.58	35.94	78.32	20.86
D-limonene	15	4.45	4.47	9.32	4.27	4.20	10.54	57.32	7.22

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE$_1$	mSE$_2$	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
linalool	15	3.88	4.32	7.24	5.63	4.13	13.86	63.29	10.49
linoleic acid	71	4.59	4.56	7.18	28.07	20.02	38.05	105.64	38.00
linoleic acid methyl ester	21	1.89	1.94	15.74	7.44	3.30	16.35	77.97	37.24
α-linolenic acid	56	2.08	2.04	5.85	26.33	18.69	36.15	102.41	32.29
γ-linolenic acid	142	4.66	4.25	7.79	16.90	8.37	26.40	92.13	36.36
γ-linolenic acid ethyl ester	41	6.14	6.38	6.31	22.63	13.68	32.31	98.89	23.99
γ-linolenic acid methyl ester	52	6.62	6.59	13.41	10.20	4.68	19.17	82.00	19.94
L-menthone	23	3.42	3.42	5.18	7.36	6.71	15.93	65.04	19.79
methanol	10	3.78	4.04	19.71	6.87	51.52	26.96	35.02	18.17
2-methylanisole	15	8.90	8.08	9.67	16.19	23.02	26.90	72.34	22.89
4-methylanisole	15	16.75	15.85	17.52	24.50	31.83	35.98	84.67	31.81
1-methylnaphthalene	11	16.82	14.73	37.22	45.23	53.95	58.66	115.29	29.56
monoolein	11	4.28	3.82	6.55	32.29	21.50	42.93	116.58	43.52
myristic acid ethyl ester	16	4.90	4.68	3.62	15.85	9.08	24.84	85.27	23.65
myristoleic acid	42	8.26	7.68	5.68	22.90	14.76	32.51	98.00	31.43
myristoleic acid methyl ester	81	10.94	10.97	10.43	19.53	12.73	28.83	93.69	14.85
naphthalene	114	9.48	10.34	10.71	13.04	19.28	21.47	63.14	9.27
1-naphthol	11	12.69	16.11	5.77	0.39	5.67	9.17	48.49	4.60
2-naphthol	16	17.44	20.64	7.84	2.46	5.02	7.67	45.23	10.71
2-nitroanisole	15	9.52	6.62	30.85	35.55	47.49	49.02	98.39	30.58

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE$_1$	mSE$_2$	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
nitrobenzene	23	5.00	3.00	25.45	26.09	42.77	40.14	81.24	19.01
3-nitrotoluene	15	2.66	2.31	22.65	26.33	38.46	39.13	84.26	18.41
n-nonane	5	3.17	3.28	29.75	22.54	21.49	16.10	17.68	21.11
n-octane	5	2.62	2.73	27.16	20.95	18.53	14.14	18.95	20.36
oleic acid	19	5.87	5.89	7.41	28.09	19.71	38.09	106.18	40.02
oleic acid ethyl ester	5	7.87	8.25	16.55	42.53	31.64	53.87	132.03	29.14
oleic acid methyl ester	21	7.10	7.58	17.48	43.85	33.52	55.19	133.02	28.61
palladium(II) acetylacetonate	125	3.17	12.54	21.93	32.80	36.33	44.15	100.26	38.05
palmitic acid ethyl ester	17	3.00	2.84	1.90	19.94	11.63	29.35	93.78	28.90
n-pentane	5	4.97	4.99	14.15	11.94	2.97	2.87	28.13	12.10
2-pentanone	23	2.90	2.44	4.45	4.95	16.85	15.50	50.45	2.27
3-pentanone	46	5.34	4.88	4.65	4.90	15.85	14.37	48.79	4.22
n-pentylbenzene	31	2.62	2.65	4.80	14.69	16.85	24.33	73.70	17.17
phenanthrene	25	12.86	14.74	7.59	8.72	10.53	16.03	61.22	5.38
phenol	109	5.91	4.06	21.20	17.97	39.93	33.07	66.34	10.36
phenylacetic acid	16	3.77	2.22	4.25	12.95	16.60	22.72	69.79	15.84
phenylacetylene	15	7.65	6.60	16.98	19.02	32.55	31.66	72.34	16.04
phenylbutazone	78	4.71	5.21	8.18	15.80	7.66	25.06	89.10	32.68
1-phenyldodecane	15	12.72	12.37	13.38	35.46	28.08	45.96	115.88	47.18
1-phenylethanol	15	11.55	9.12	24.92	29.04	40.91	41.99	88.54	25.33

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE$_1$	mSE$_2$	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
2-phenylethanol	15	12.79	10.48	26.44	30.45	42.67	43.59	90.46	26.79
2-phenylethyl acetate	15	13.54	11.64	8.63	22.22	21.45	32.02	87.91	36.37
1-phenylhexane	15	3.97	3.64	7.16	19.26	19.67	28.99	82.26	23.78
phenylmethanol	15	12.03	10.14	28.01	28.91	45.59	43.17	85.52	22.63
1-phenyloctane	15	3.49	3.40	4.12	18.65	16.12	27.98	84.27	27.35
3-phenylpropyl acetate	15	12.89	11.15	7.12	21.63	18.93	31.18	89.00	38.05
α-pinene	15	5.37	5.35	5.22	13.38	17.32	23.25	70.23	9.28
β-pinene	15	7.98	7.93	3.61	8.63	12.20	17.68	62.30	5.08
2-phenyl-1-propanol	15	12.99	10.55	25.01	31.71	40.36	44.06	94.72	30.05
3-phenyl-1-propanol	15	10.55	7.99	22.62	29.31	37.66	41.40	91.29	27.20
1-propanol	17	7.56	7.63	20.58	15.04	40.74	31.17	60.29	4.49
2-propanol	18	3.79	3.87	13.26	8.46	31.92	23.41	51.47	7.64
i-propylbenzene	36	4.22	4.28	3.75	6.55	12.80	16.24	57.73	7.55
n-propylbenzene	60	7.29	7.24	13.29	17.28	23.56	27.35	72.81	8.03
pyrene	21	5.47	7.21	9.75	6.51	3.86	13.38	64.89	20.08
squalene	5	6.02	6.28	13.56	11.21	3.78	20.60	85.24	38.21
stearic acid ethyl ester	17	5.47	4.21	2.89	20.71	11.22	30.36	96.97	25.70
styrene	15	6.02	5.48	13.86	16.73	28.71	28.77	69.79	14.72
n-tetradecane	5	9.18	9.74	30.00	17.78	21.27	11.41	29.72	12.24
tetrahydrofuran	15	5.43	5.44	16.67	12.92	35.09	27.75	58.71	10.90

Table 2 (*Continued*)

		New models†		Models from the literature†					
		mSE$_1$	mSE$_2$	WC	TC	Sch	LR	RD	LT
Solute	NDP	(Eqs. (2) + (13))	Eqs. (5), (13), and (3) – (4))	(Eq. (6))	(Eq. (8))	(Eq. (9))	(Eq. (10))	(Eq. (11))	(Eq. (12))
thenoyltrifluoroacetone	15	15.02	13.61	30.20	41.38	45.60	53.55	112.83	47.64
α-tocopherol	82	13.11	13.90	11.99	13.67	4.00	23.35	89.77	27.17
toluene	35	3.88	3.83	6.09	6.86	19.41	17.92	53.47	4.46
triarachidonin	27	5.67	5.50	17.49	20.63	8.39	34.89	116.86	70.26
trierucin	101	5.88	6.13	13.57	31.19	14.68	48.33	140.57	82.31
trifluoroacetylacetone	15	5.30	6.00	3.74	9.06	15.88	19.21	61.49	11.17
1,3,5-trimethylbenzene	34	5.64	5.54	10.63	16.91	24.00	27.73	73.26	15.52
trinervonin	38	4.98	5.19	16.62	27.91	12.12	45.38	136.63	83.21
triolein	14	9.02	6.31	16.34	22.42	10.40	36.93	120.20	54.00
ubiquinone CoQ10	80	3.40	3.37	13.90	23.98	8.60	37.98	120.85	71.55
n-undecane	5	3.44	3.50	33.77	24.86	25.91	18.89	16.12	21.81
vanillin	15	7.93	4.46	12.64	21.65	26.02	32.26	82.53	24.63
vitamin K$_1$	17	11.18	10.99	27.24	4.02	11.90	9.52	72.52	31.21
vitamin K$_3$	22	5.46	8.10	9.59	7.18	6.78	12.86	61.01	12.03
m-xylene	12	12.46	12.35	27.07	31.70	43.21	44.75	92.80	16.46
5-*tert*-butyl-*m*-xylene	31	2.27	2.30	8.49	5.79	3.60	14.06	64.71	19.40
p-xylene	7	4.94	4.94	4.28	6.13	15.06	16.37	55.10	4.52

†mSE$_1$ = New *modified Stokes-Einstein*-1 model; mSE$_2$ = New *modified Stokes-Einstein*-2 model; WC = Wilke-Chang; TC = Tyn-Calus; Sch = Scheibel; LR = Lusis-Ratcliff; RD = Reddy-Doraiswamy; LT = Lai-Tan.

Though mSE_1 and mSE_2 perform very similarly, in 11 systems the first model provides AARDs at least 2.02% lower. On the other hand, mSE_2 offers 14 AARDs inferior by 2.05%.

A complementary comparison between the new models and those of Wilke-Chang, Tyn-Calus, Scheibel, Lusis-Ratcliff, Reddy-Doraiswamy, and Lai-Tan is shown in Table 3, where the following statistics are listed for each equation: global AARD, maximum AARD, minimum AARD, and the standard deviation of AARDs (σ_{AARD}) as a measure of their dispersion around the average. It is evident that the mSE_1 and mSE_2 equations offer an enhanced performance when compared to the remaining ones: global AARDs of 6.38% and 6.75% (without *n*-alkanes), and 3.66% and 3.77% (for *n*-alkanes), respectively, against deviations from 12.17% (Wilke-Chang) to 79.34% (Reddy-Doraiswamy). Not only the global averages but also the intervals between maximum and minimum AARDs are much smaller in the case of mSE_1 and mSE_2, which highlights their reliability. Furthermore, the computed standard deviations are four to six times inferior in our case, which implies that mSE_1 and mSE_2 models behave equally well for all systems of database. Hence, they may be assumed as trustworthy models for the prediction of tracer diffusion coefficients of solutes in supercritical CO_2, particularly for unknown systems at any condition.

Table 3. Comparison of the performance achieved by the new models and by the expressions adopted for comparison: global, maximum and minimum errors (AARD), and standard deviation of the AARDs of all systems.

Model	$AARD_{global}$	$AARD_{min}$	$AARD_{max}$	σ_{AARD}
mSE_1	6.38	1.89	26.17	4.12
mSE_2	6.75	1.94	26.40	4.28
mSE_1 for *n*-alkanes	3.66	1.13	9.18	2.31
mSE_2 for *n*-alkanes	3.77	1.25	9.74	2.45
Wilke-Chang	12.17	1.67	42.40	8.44
Tyn-Calus	17.01	0.39	49.65	9.69
Scheibel	19.04	0.94	63.36	13.22
Lusis-Ratcliff	27.32	2.87	62.37	11.69
Reddy-Doraiswamy	79.34	16.12	140.57	24.19
Lai-Tan	25.82	2.27	83.21	14.94

mSE_1 = New *modified Stokes-Einstein*-1 model; mSE_2 = New *modified Stokes-Einstein*-2 model

Taking account of the individual AARDs of Table 2, one may additionally check that: *i*) the mSE$_1$ model provides better results than mSE$_2$ in 53 systems. The average deviation for this set of systems is 6.29%, which is only 0.09% inferior to the global AARD of the whole database (Table 3: 6.38%). *ii*) the mSE$_2$ equation performs better than mSE$_1$ in 94 systems, for which the average error is 5.82%, *i.e.* only 0.93% smaller than the global AARD obtained for the complete database (Table 3: 6.75%). Such findings reinforce even more the consistent and accurate behaviour of both models, which is fundamental for their application in pure predictions.

In Figure 2, the tracer diffusivities calculated by mSE$_1$, mSE$_2$, Wilke-Chang and Lai-Tan expressions are plotted against the experimental values. The Wilke-Chang model is chosen because it provides the best results among all hydrodynamic models of the literature (Table 3: AARD = 12.17%); the Lai-Tan equation is selected since it is much more recent and is specific for supercritical carbon dioxide systems. In the whole, Figure 2 points out the good distribution of mSE$_1$ and mSE$_2$ points along diagonal, in contrast to the biased cloud corresponding to the Wilke-Chang and mainly to the Lai-Tan diffusivities, despite being SC-CO$_2$-specific. These observations emphasize once again the accuracy of our mSE$_1$ and mSE$_2$ models. In Figure 3, a similar plot is illustrated for the *n*-alkanes group, which corroborates the excellent results provided by the new models.

The differences between our models and those from literature can be more explored and analysed in terms of their dependences on the properties of solute. According to the Wilke-Chang equation, D_{12} is a linear function of $V_{\mathrm{bp},2}$ in log-log coordinates (see Eq. (6)). However, as Figure 4.a illustrates, this trend is not strictly followed by a set of data from 65 systems at 313.15 and 333.15 K. In the case of Lai-Tan correlation (Eq. (12)), $D_{12} \propto 1/\left(V_{\mathrm{c},2}\right)^{1/3}$, though Figure 4.b points out the experimental data do not obey such relation. Finally, the new models mSE$_1$ and mSE$_2$ do describe the diffusive phenomenon accurately, as their interrelation $D_{12} \propto 1/\left(M_2 V_{\mathrm{bp},2}\right)^{\beta}$ is truly followed by the same data collected (see Figure 4.c). It is worth noting that the introduction of the solute molecular weight is essential to describe D_{12} correctly, since it is the core difference between them mSE$_1$ or mSE$_2$ and the Wilke-Chang equation.

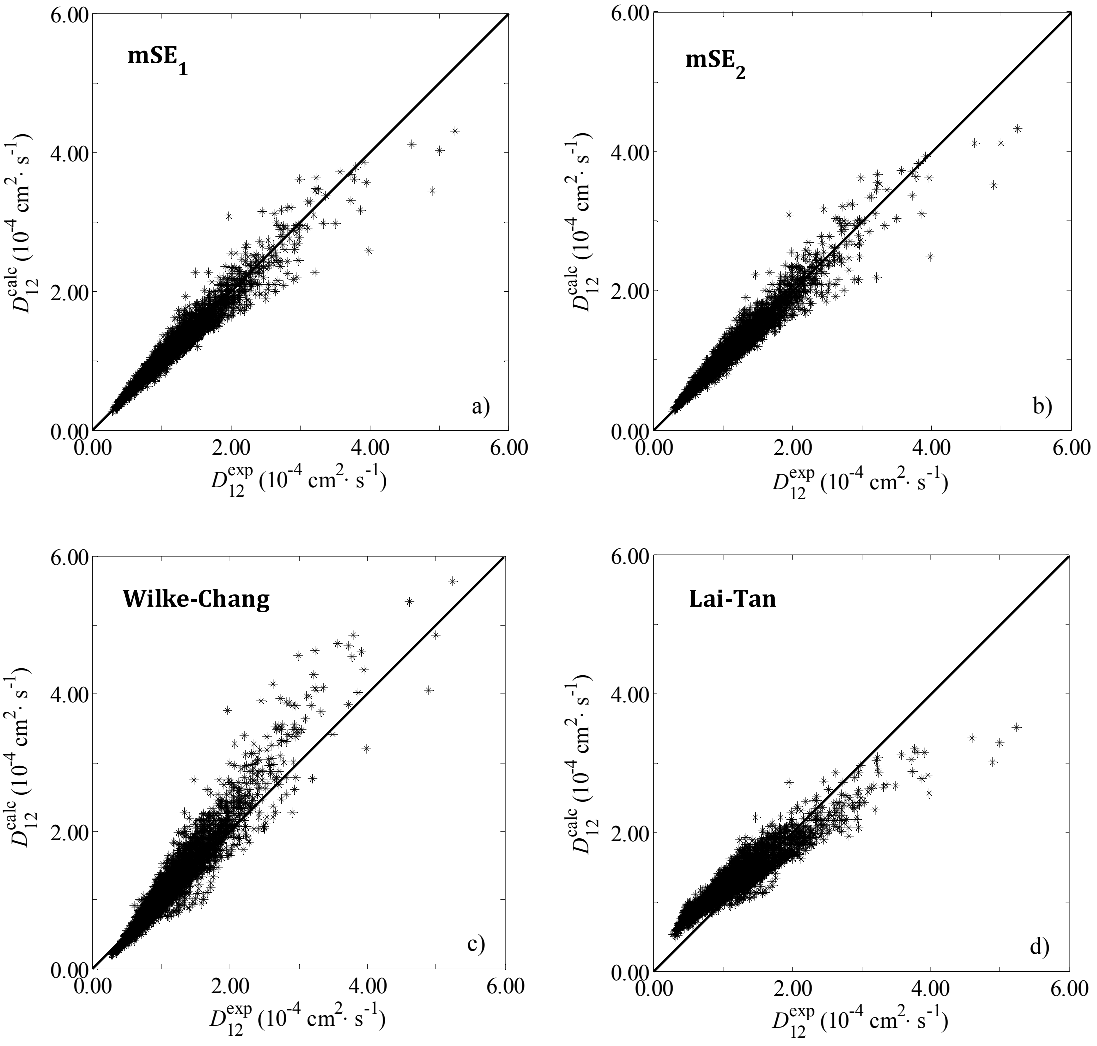

Figure 2. Calculated *versus* experimental tracer diffusivities for the: a) *modified Stokes-Einstein*-1, b) *modified Stokes-Einstein*-2, c) Wilke-Chang, and d) Lai-Tan equation.

To further examine the behaviour of our models against those adopted for comparison, several isotherms for very different systems are graphed in Figure 5: ethyl ester of arachidonic acid, 1,3-divinylferrocene, ferrocene, and ubiquinone CoQ10 in carbon dioxide. For each experimental isotherm, the calculated results are also drawn: mSE$_1$ and mSE$_2$ are the full lines (since both equations are equally good, their plots are overlapped), and Lai-Tan and Wilke-Chang are the large and small dashed lines, respectively. As expected in advance, in view of the previous discussion, our models accompany accurately the experimental data, while significant deviations arise with Wilke-Chang and, especially, Lai-Tan equations. Similar results may be found for the remaining mixtures, and are in accordance with the AARDs obtained before (see Tables 2 and 3).

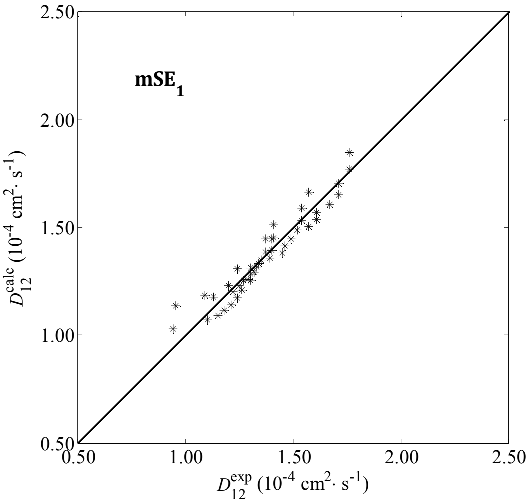

Figure 3. Calculated *versus* experimental tracer diffusivities of *n*-alkanes for the *modified Stokes-Einstein*-1 model. Similar plot is obtained with *modified Stokes-Einstein*-2 equation.

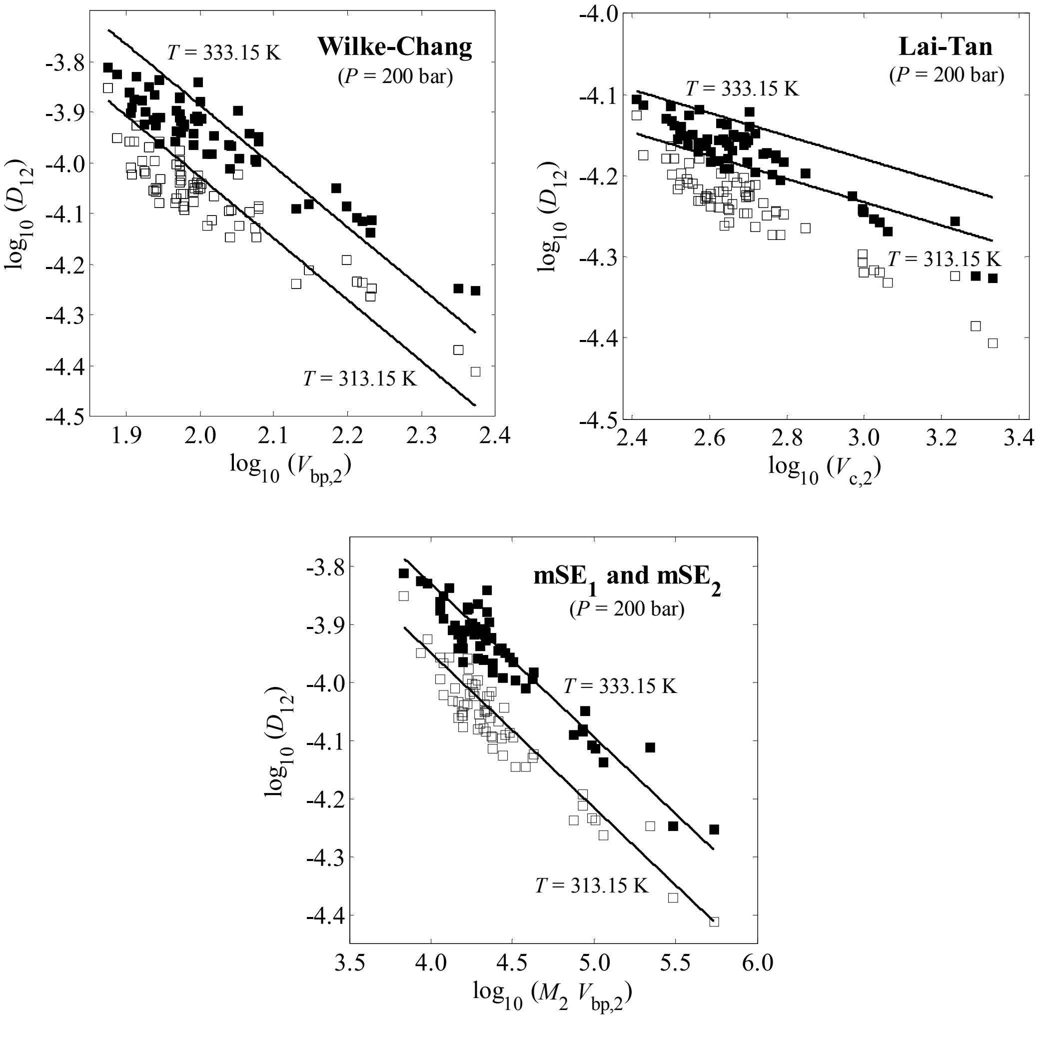

Figure 4. Dependence of D_{12} upon the solute properties explicitly expressed by each model: a) $V_{bp,2}$ for Wilke-Chang, b) $V_{c,2}$ for Lai-Tan, and c) $M_2 \, V_{bp,2}$ for mSE$_1$ and mSE$_2$. Symbols: experimental data for 65 systems from database; Full lines: calculated results.

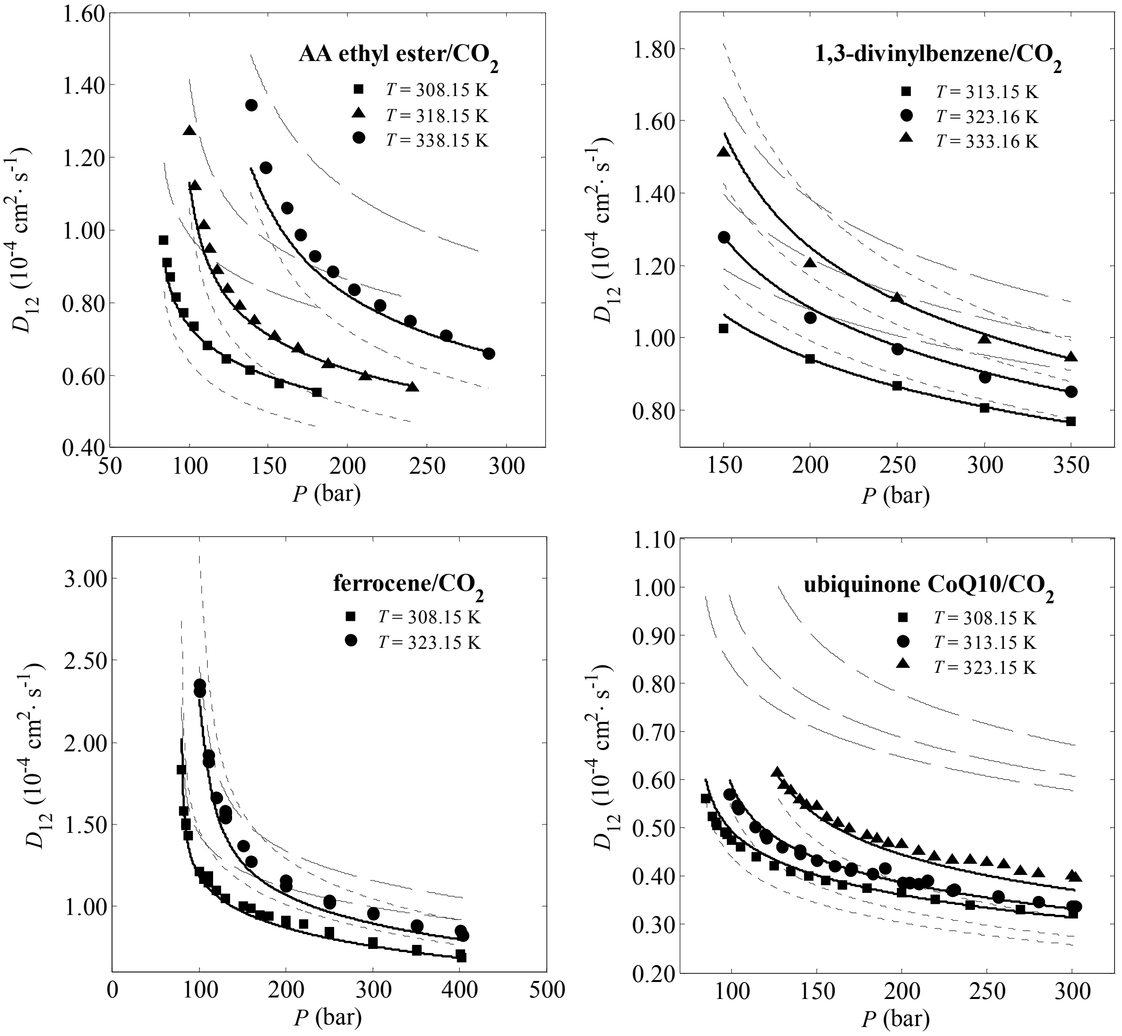

Figure 5. Experimental and calculated tracer diffusion coefficients at constant temperatures: a) ethyl ester of arachidonic acid (AA), b) 1,3-divinylbenzene, c) ferrocene, d) ubiquinone CoQ10. Models: (—) mSE_1 and mSE_2, (···) Wilke-Chang and (– –) Lai-Tan.

4.PVIII.6. Conclusions

In this work, two modified Stokes-Einstein models were proposed with the main objective to provide accurate predictions of tracer diffusion coefficients in supercritical carbon dioxide. The first one is denoted by mSE_1 and is given by Eqs. (2) + (13), while the second one, called mSE_2, corresponds to Eqs. (5) + (13) + (3) – (4); the three universal constants embodied in their equations are listed in Table 1. The validation of both models was accomplished with the largest diffusivities database (156 systems and 4425 data points), and provided very accurate results for the whole database over wide ranges of pressure and temperature: the global deviations are only 6.38% and 6.75%, respectively. Six predictive correlations frequently adopted in the literature were selected for comparison, but higher errors were obtained: Wilke-Chang, 12.17%; Tyn-Calus, 17.01%; Scheibel, 19.04%; Lusis-Ratcliff, 27.32%; Reddy-Doraiswamy, 79.34%; Lai-Tan, 25.82%. After careful analysis of our results both mSE$_1$ and mSE$_2$ models can be recommended to compute reliable and accurate predictions of tracer diffusivities, even for unknown systems.

Nomenclature

A', A''	Universal constants in Eqs. (2) and (5)
AARD	Average absolute relative deviation, %
D_{12}	Tracer diffusion coefficient
k_{B}	Boltzmann constant
LJ	Lennard-Jones
LR	Lusis-Ratcliff equation
LT	Lai-Tan equation
M	Molecular weight
mSE$_1$	*Modified Stokes-Einstein*-1 model
mSE$_2$	*Modified Stokes-Einstein*-2 model
NDP	Number of data points
P	Pressure
$\mathbf{P}_i$	Parachor of component i
r	Radius of the molecule
RD	Reddy-Doraiswamy equation
SC-CO$_2$	Supercritical carbon dioxide
SCF	Supercritical fluid
SFE	Supercritical fluid extraction
Sch	Scheibel equation
SMB	Simulated Moving Bed
T	Absolute temperature
TC	Tyn-Calus equation
WC	Wilke-Chang equation

Greek letters

α', α''	Universal constants in Eqs. (2) and (5)
β', β''	Universal constants in Eqs. (2) and (5)
ϕ_1	Dimensionless association factor in Wilke-Chang equation
η_1	Solvent viscosity
σ	Surface tension

Subscripts

1	Solvent
2	Solute
12	Binary
bp	Boiling point
c	Critical
i	Molecule i
r	Reduced property

Superscripts

calc	Calculated value
exp	Experimental value
TC	Group contribution method of Tyn-Calus

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Part II

EXPERIMENTAL SECTION

5. Fundamentals of Experimental Measurements of Diffusivities

The binary diffusion coefficient, D_{12}, has a huge importance in research and industry, being indispensable for optimum process designs and simulations. Its measurement in gas, liquid and supercritical fluids can be accomplished by different techniques. In this chapter some of the methods available in literature are presented, like photon correlation spectroscopy, geometric methods, nuclear magnetic resonance (NMR), and two chromatographic techniques (chromatographic peak broadening (CPB) and chromatographic impulse response (CIR) methods).

5.1. Photon Correlation Spectroscopy

This method involves the analysis of the scattered light spectrum of the target binary mixture, and it is based on the following principles: when a monochromatic light is focused in a fluid it disperses due to the presence of optical inhomogeneities due to fluctuations in the local dielectric constant, $\delta\omega(r,t)$. This phenomenon takes place at microscopic level, where regions with different local densities in the fluid are observed. Owing to the presence of clusters, even where the fluid is in equilibrium, fluctuations in dielectric constant occur. These fluctuations in supercritical conditions become mainly important, since very near the critical point the fluid becomes quite opalescent. In a binary mixture, $\delta\omega(r,t)$ is related with fluctuations in the local thermodynamic quantities, namely the pressure, temperature, and concentration [1]:

$$\delta\omega(r,t)=\left(\frac{\partial\omega}{\partial P}\right)_{T,C}\delta P(r,t)+\left(\frac{\partial\omega}{\partial T}\right)_{P,C}\delta T(r,t)+\left(\frac{\partial\omega}{\partial C}\right)_{P,T}\delta C(r,t) \qquad (5.1)$$

These fluctuations are time-dependent and modify the incident field, make light to be scattered, which in turn provides information about transport properties and the shape of the spectrum. Temperature and concentration fluctuations decay exponentially with time and are given by [1]:

$$\delta T(r,t) = \delta T(\Gamma,0)\exp\left(-\chi\,\Gamma^2 t\right) \tag{5.2}$$

$$\delta C(r,t) = \delta C(\Gamma,0)\exp\left(-D_{12}\,\Gamma^2 t\right) \tag{5.3}$$

wherein $\Gamma = (4\pi n/\lambda_{\mathrm{rad}})\sin(\theta/2)$, and n is the index of refraction, λ_{rad} is the incident wavelength of the incident light under vacuum, θ is the scattering angle, $\chi = \lambda/(\rho_1 c_{\mathrm{p}})$ is the thermal diffusivity; λ, ρ_1, and c_{p} are the thermal conductivity, density, and the specific heat of solution, respectively; and D_{12} is the binary diffusion coefficient. From the two previous equations it is possible to verify that both χ and D_{12} can be calculated from the fluctuations decay rate in the dielectric constant [2-3].

The application of this method to measure diffusivities has been widely used in pure fluids, especially in gases. In what concerns supercritical fluids, only the works from Saad and Gulari [2-4], who measured diffusion coefficients of *n*-heptane, *n*-decane, and benzene in carbon dioxide along isochors at concentrations inferior than 5% of hydrocarbons, is reported in literature. These authors obtained results with errors of approximately 6%.

With this technique there is no disturbance of the thermodynamic equilibrium, it does not involve the measurement of gradients and fluxes, which are challenging to be accurately obtained at high pressures, and it also allows viscosities in dense fluids to be measured. However, the signal-to-noise ratio must be high and the refraction indices of the components must differ at least 5 – 10%. Besides, there is currently no theoretical model that interprets the relationship between the radiation probe and the molecular motion. Another disadvantage is the high costs of this type of equipment [5].

5.2. Geometric Methods

These methods are essentially employed in the determination of diffusion coefficients of solid substances. They measure the velocity at which the solute diffuses from a cell with finite volume to an external layer of solvent, thus implying the existence of an initial concentration gradient. The experimental apparatus used in these techniques can have multiple variants: *e.g*. cells with different shapes and geometries, concentration gradients can be time-independent or not, and the solvent can be in steady state in the cell, or can cross it.

In 1962, Tsekhanskaya and Iomtev [6], using this technique, determined diffusion coefficients of solid substances in supercritical fluids. The method is very simple and D_{12} is determined without the need to analyze the supercritical fluid phase. In this technique, a pure solid, which it was compressed inside the cell, is dissolving and diffusing into a supercritical fluid, and the diffusivities are calculated by the weight loss of the solid in a certain period of time. The authors reported diffusivities with uncertainties between 2 and 8%.

Debenedetti and Reid [7] employed a similar technique which involves a fully developed laminar flow in a horizontal rectangular duct, wherein the bottom surface of the channel is covered with the desired solute. They determined binary diffusion coefficients of low volatile compounds (naphthalene, benzoic acid and 2-naphthol) in supercritical carbon dioxide, and sulphur hexafluoride. The authors made an exhaustive analysis of mass transfer, but the diffusivities were estimated to have an absolute error of 22%. Extra precautions are necessary during the measurement of diffusion coefficients, since the relative importance of convection is about two orders of magnitude higher in supercritical fluids than in liquids.

Knaff and Schlünder [8] developed a pseudo-steady state solid dissolution method to measure D_{12} in supercritical fluids. They studied systems containing sublimable solids, such as naphthalene and caffeine, in supercritical carbon dioxide, although this was a technique more common in liquid systems. By manipulating the conservation law and kinetics as well as boundary conditions, the binary diffusivity can be related with geometric parameters and properties of the substances involved as follows:

$$D_{12} = \frac{\rho_2 \left(h_{\mathrm{f}}^2 - h_{\mathrm{i}}^2\right)}{2\left(\mathrm{M}_2/\mathrm{M}_1\right)\rho_1 Y^* t} \qquad (5.4)$$

where ρ_1 and ρ_2 represent the densities, h_i and h_f are distances from interface from the capillary entrance to the surface of the solid solute at the beginning and end of the experiments, Y^* is the saturated solubility, and t is the time of each experiment. Knaff and Schlünder [8] obtained diffusivities, for their systems studied, with errors approximately 11%. Catchpole and King [9] using this technique determined diffusion coefficients of benzoic acid and naphthalene in supercritical carbon dioxide, near critical point.

Higashi *et al.* [10-11] measured the D_{12} data of naphthalene, 2,6-dimethyl-naphthalene, and 2,7-dimethyl-aphthalene in supercritical carbon dioxide and reported errors in their values of D_{12} inferior to 16%.

Baker and Trebble [12] designed a new gravimetric analysis apparatus to measure directly the mass transfer rate of solid solutes into supercritical fluids, using a miniature thin film strain gauge load cell placed inside an extraction vessel, which quantify the mass of solid solute suspended in a solvent flowing continuously. They obtained diffusivities of naphthalene in supercritical carbon dioxide in a good agreement with data published.

Ozguler *et al.* [13] tested the Stefan tube applicability in the diffusion coefficients measurements of nonvolatile solids in supercritical fluids. Once again, these authors obtained D_{12} values of naphthalene in supercritical carbon dioxide in a good agreement with literature data available.

5.3. Nuclear Magnetic Resonance

This technique uses nuclear magnetic resonance (NMR) spectroscopy and has been applied to measure diffusion coefficients in supercritical fluids, although at the beginning it was widely carried out in systems at ambient temperature and/or at atmospheric pressure. From the relaxation times of the nuclear magnetic resonance important information can be obtained, not only about molecular interactions, but also site-specific information on intramolecular motions. Using this technique, Baker *et al.* [14-15], determined the self-diffusion coefficients of supercritical toluene-D_8 and supercritical ethylene, and Jonas [16] measured self-diffusivities in wide ranges of temperatures

(223.15 to 623.15 K) and pressures (0 to 5000 bar), maintaining a high homogeneity in the magnetic field. The errors reported for D_{12} were inferior to 10% but can be reduced to 4% [5]. In 1989, Lamb *et al.* [17] measured diffusion coefficients of naphthalene and naphthalene-D_8 in supercritical ethylene and in supercritical carbon dioxide by this technique.

Although NMR spectroscopy presents itself an enormous potential for the measurement of diffusion coefficients, the reason for not being quite applied for this specific purpose relies on equipment costs, which are considerably high.

5.4. Chromatographic Method

This method has been broadly used to measure diffusion coefficients, not only in pure solvents but also in mixtures. It is based on the fundamental work formulated by Taylor [18-20], and later developed and formalized by Aris [21], whose purpose was a description of a solute dispersion in a laminar flow of mobile phase through a circular tube. Giddings and Seager [22] utilized primarily this methodology for obtaining diffusion coefficients in gaseous mixtures at low pressure. Subsequently, it has been extended to liquid and supercritical systems. In last decades, this technique found a huge application in measurement of diffusivities in supercritical systems.

The procedure is considered a type of transient response method, where a delta-like pulse of solute is injected into a flowing solvent, and the response is measured at the outlet. It provides several advantages over other methods, which are conducted under steady state, because the measurement of transport properties can be achieved through small gradients of driving forces, as small changes in concentration, and it requires less time when compared with steady state methods. Thereby, the chromatographic method can be succinctly described as an accurate methodology (errors around 5%, with fine reproducibility), and its execution is fast (frequently, within one and two hours). Figure 5.1 presents a schematic apparatus used for supercritical fluid chromatography (SFC).

In this work two different chromatographic techniques available in literature are described: the chromatographic peak broadening (CPB), and the chromatographic impulse response (CIR) methods. Experimentally, the main difference between both techniques is the type of column, uncoated in case of CPB, while coated with a polymer film in CIR method.

5.4.1. Chromatographic Peak Broadening

The chromatographic peak broadening method (CPB), also called Taylor's method, has been extensively used to measure binary diffusion coefficients, D_{12}, of solutes in pure/mixed solvents by analysing the response of an uncoated capillary column to an impulse of solute injected in a laminar flow of solvent. A brief description of the CPB method, and the main equations that allow the calculation of the diffusion coefficient from an experimental run, will be presented.

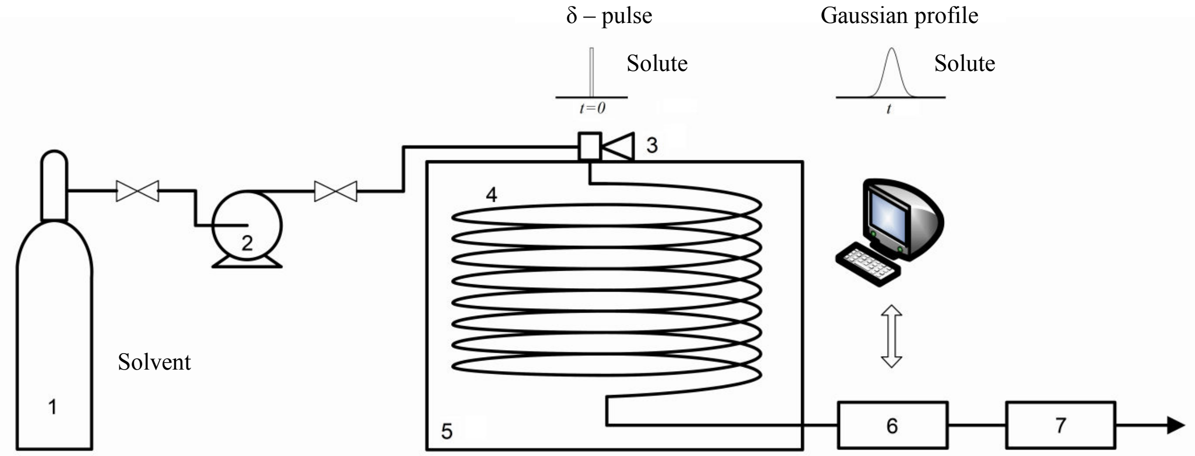

Figure 5.1. Simplified diagram of the apparatus used in supercritical fluid chromatography: 1) solvent cylinder, 2) pump, 3) injector, 4) diffusion column, 5) oven or bath at constant temperature, 6) detector, and 7) backpressure regulator (BPR) or restrictor.

When a solute is pulse-loaded into a fully laminar flow of solvent, the pulse broadens owing to the combined presence of convection in the axial direction due to the velocity gradient in the solvent and diffusion in the radial direction. The solute mass balance inside a column of circular cross section is described by the following equation:

$$D_{12}\left(\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\partial r}+\frac{\partial^2 c}{\partial z^2}\right)=\frac{\partial c}{\partial t}+2u_0\left(1-\frac{r^2}{R^2}\right)\frac{\partial c}{\partial z} \tag{5.5}$$

where c is the solute concentration, u_0 is the average linear velocity of the solvent, R is the inner radius of the dispersion tube, r and z represent the radial and axial coordinates, respectively, and t is the time.

The initial and boundary conditions are given by:

$$c = \frac{m}{\pi R^2}\,\delta(z), \quad \text{at} \quad t = 0 \tag{5.6}$$

$$\frac{\partial c}{\partial r} = 0, \quad \text{at} \quad r = 0 \text{ and } r = R \tag{5.7}$$

$$c = 0, \quad \text{at} \quad z = \pm\infty \tag{5.8}$$

where m is the total mass of solute injected. The average concentration per cross sectional area of the tube is defined by:

$$C(z,t) = \frac{2}{R^2}\int_0^R c(r,z,t)\, r\, dr \tag{5.9}$$

Taylor [18] and Aris [21] have shown that the asymptotic behaviour of Eq. (5.5) is equivalent to a axial dispersion model after applying Eq. (5.9) for calculating the solute distribution along the tube on Eq. (5.5):

$$\frac{\partial C_{\text{app}}}{\partial t} = D\frac{\partial^2 C_{\text{app}}}{\partial z^2} - u_0\frac{\partial C_{\text{app}}}{\partial z} \tag{5.10}$$

being C_{app} an average concentration of solute, and D an apparent axial dispersion coefficient. In the previous equation the first term on the right hand side corresponds to a diffusive mechanism and the others are related with a plug flow in unsteady state. When the dispersion coefficient combines both effects of parabolic axial velocity profile and the radial molecular diffusion, the asymptotic equivalence is attained according to:

$$D = D_{12} + \frac{R^2 {u_0}^2}{48 D_{12}} \tag{5.11}$$

The combination of these two distinct phenomena in a unique simplified model, introduces an approximation, since its validity is restricted to columns of infinite length. From Eq. (5.11) it is possible to observe that the second term on the right hand, $R^2 u_0^{\ 2} / 48 D_{12}$, which has an inverse ratio with respect to D_{12}, has a huge impact in the dispersion, and as long as the value of this term is greater than D_{12}, any increase on diffusion coefficient will lead to a dispersion reduction, or even its elimination.

Then, the initial and boundary conditions are now given by:

$$C_{\text{app}} = \frac{m}{\pi R^2} \delta(z), \qquad \text{at} \qquad t = 0 \tag{5.12}$$

$$C_{\text{app}} = 0, \qquad \text{at} \qquad z = \pm\infty \tag{5.13}$$

The solution of Eqs. (5.10) – (5.13) is expressed as:

$$C_{\text{app}}(z,t) = \left(\frac{m}{\pi R^2} \right) \frac{1}{2\sqrt{\pi D t}} \exp\left[-\frac{(z - u_0 t)^2}{4 D t} \right] \tag{5.14}$$

From the Taylor-Aris diffusive phenomenon, that takes into account the intrinsic symmetry to the axial dispersion, a material that is put in position $z = 0$ appears as a Gaussian peak in position $z = L$, far from the injection point. Mathematically, D_{12} can be obtained from the variance of the response curve, σ^2, which is given by:

$$\sigma^2 = \frac{2 D L}{u_0} = \frac{2 D_{12} L}{u_0} + \frac{R^2 u_0 L}{24 D_{12}} = L H \tag{5.15}$$

where H is the height of the theoretical plate. The first term in third member represents the dispersion due to the axial diffusion, and the second one takes into account the peak opening because of the parabolic velocity profile and the diffusion in radial direction.

Levenspiel and Smith [23] proved that the concentration profile, which results from the dispersion of the initial impulse of solute, becomes particularly Gaussian, if the following inequality is observed:

$$\frac{D}{u_0 L} < 0.01 \tag{5.16}$$

It is necessary to note that Eqs. (5.15) and (5.16) have been derived for the case where a straight tube was employed. In practice, the column is coiled in order to be placed in a constant temperature bath or oven. In this case, the Taylor-Aris model is a function of two dimensionless numbers, Reynolds (Re) and Schmidt (Sc), and the geometric factor $\zeta = R_\mathrm{c}/R$, also named curvature ratio, where R_c is the coil radius, and R the internal radius of the column. Under certain conditions Re and ζ are not independent variables, but a combination of both ($\mathrm{De} = \mathrm{Re}/\sqrt{\zeta}$, Dean number) that affects the dispersive behaviour, by producing secondary flow in the column. These secondary flow effects inside the column can be neglected for high values of curvature ratio [24-26], since:

$$\mathrm{De}\sqrt{\mathrm{Sc}} < 10 \tag{5.17}$$

Disturbances due to a decrease in pressure or temperature between the column and the detector are negligible when [27]:

$$u_0 L/D > 1000 \tag{5.18}$$

Fulfilled the constraints given by Eqs. (5.16) and (5.17), the binary diffusion coefficient, D_{12}, can be calculated by rearranging Eq. (5.15):

$$D_{12} = \frac{u_0}{4}\left[H \pm \sqrt{H^2 - \frac{R^2}{3}}\right] \tag{5.19}$$

As it is possible to observe, this equation has two different solutions for D_{12}, but only one of them possesses physical meaning. Giddings and Seager [22] have shown that when the solvent linear velocity exceeds the value of velocity that minimizes H, $u_{0,\mathrm{opt}} = \sqrt{48}\,(D_{12}/R)$, the diffusivity should be determined by the negative root of Eq. (5.19). Generally, the optimum velocities in supercritical fluids and liquids are very small, being easy to reach higher values.

The height of the theoretical plate, according Lauer *et al.* [28], can be determined by the following equation:

$$H = \frac{u_0^2 \, W_{0.607}^2}{L} \tag{5.20}$$

where $W_{0.607}$ is the half width at 60.7% of the peak height, in time units. Other authors used another approach to calculate the height of the theoretical plate, which involves the measurement of the width at 50% of the peak height.

Further mathematical techniques can be used to analyze the experimental data in order to extract the diffusivities, *e.g.* the moment method, and the curve fitting method. The results obtained by the moment method are similar to the graphic peak width methodology, since the equation for the variance, σ^2, which corresponds to the second moment, is equal to the Eq. (5.15). Both methods have been extensively used to obtain binary diffusion coefficients, however it has been reported that the curve fitting methodology is more accurate than the others [29-30]. In the curve fitting method, D_{12} is obtained so as to minimize the root mean square error, ε , defined by:

$$\varepsilon = \left\{ \frac{\int_{t_1}^{t_2} \left[C_{\mathrm{exp}}(t) - C_{\mathrm{app}}(L,t) \right]^2 dt}{\int_{t_1}^{t_2} \left[C_{\mathrm{exp}}(t) \right]^2 dt} \right\}^{1/2} \tag{5.21}$$

where $C_{\mathrm{exp}}(L,t)$ is the solute concentration measured at column end, and $C_{\mathrm{app}}(L,t)$ is the calculated concentration given by the Eq. (5.14), and t_1 and t_2 are times at 10% peak height of the response curve ($t_1 < t_2$). Funazukuri *et al.* [31] established that ε values inferior to 0.01 indicate a good fit, and acceptable when $0.01 < \varepsilon < 0.03$.

With CPB method reliable data may be obtained for non-polar and weakly polar compounds [5, 30, 32], while those for polar are limited because adsorption onto column wall originates severe peak tailing, and errors higher than 35% may even result [30, 32].

5.4.2. Chromatographic Impulse Response

In order to avoid the presence of asymmetrical peaks, Lai and Tan [33] used a capillary column comprising a inner wall coated with a polymer film of polyethylene glycol. Funazukuri *et al.* [30, 34] have adopted the same strategy, and developed the chromatographic impulse response (CIR) method that allows the simultaneous measurement of binary diffusion coefficients (D_{12}) and retention factors (k) of polar or solid or highly viscous compounds with high accuracy. Solute partial molar volumes [30] and their solubilities [35] may be additionally estimated from the retention factors.

In the CIR method, as in the CPB technique, an impulse of pulse of solute, pure or dissolved in an organic solvent, is injected into a column where the solvent moves in laminar flow, but in this case the column has an internal coating consisting of a polymer. When the mixture is injected, the solute and the organic solvent are separated chromatographically while flowing through into the column since they exhibit different retention factors, k (ratio of concentrations in the polymer phase and in the fluid phase). The presence of tailing or distortion in response curves can be minimized by an appropriate choice of the polymer coating to be used in the column [30].

The fundamental equation in this method is the same as in CPB (Eq. (5.5)), with the boundary condition given by Eq. (5.7) for $r = 0$ along with Eq. (5.8). In this case, due to the presence of a polymer film inside the column, a distinct boundary condition appears at $r = R$:

$$k\frac{\partial c}{\partial t} = -\frac{2D_{12}}{R}\frac{\partial c}{\partial r}\ , \qquad \text{at} \qquad r = R \tag{5.22}$$

where k is the retention factor, taken constant irrespective of radial and axial position in the column and time, but affected by operating conditions, such as pressure and temperature. It is assumed that at each instant the equilibrium is established between the polymer layer and the supercritical fluid that is in direct contact with the surface of the polymer [30, 34]. In this case, a linear adsorption model is considered, but other authors as Kong *et al.* [36] have analysed the CIR method considering linear and non-linear isotherms. The non-linear model considered in their work was the Langmuir, and it has been shown to be able to reproduce some tailing curves.

The initial condition in this case is given by:

$$c = \frac{m}{\pi R^2}\frac{\delta(z)}{1+k}, \qquad \text{at} \qquad t = 0 \tag{5.23}$$

The average cross section concentration, $C(z,t)$, is given by Eq. (5.9), while the approximate solution, $C_{\text{app}}(z,t)$, is:

$$C_{\text{app}}(z,t) = \left(\frac{m}{\pi R^2}\right)\frac{1}{(1+k)\sqrt{4\pi a t}}\exp\left\{-\frac{(z-Ut)^2}{4at}\right\} \tag{5.24}$$

where

$$a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{1+k}\frac{R^2 U^2}{48 D_{12}} \tag{5.25}$$

$$U = \frac{u_0}{1+k} \tag{5.26}$$

The two parameters, D_{12} and k, can be simultaneously determined by minimizing the root mean square error, ε (Eq. (5.21)). As mentioned above, an acceptable result is reached when the value of ε is inferior than 0.03, and for a good result the ε value should be inferior to 0.01 [30, 37].

Alternatively, k and D_{12} can be also obtained via the moment method, where the first and second temporal moments (mean residence time, $\bar{t}$, and variance σ^2, respectively) are expressed as:

$$\bar{t} = \frac{\int_0^\infty t\, C_{\exp}(t)\,dt}{\int_0^\infty C_{\exp}(t)\,dt} \tag{5.27}$$

$$\sigma^2 = \frac{\int_0^\infty (t-\bar{t})^2\, C_{\exp}(t)\,dt}{\int_0^\infty C_{\exp}(t)\,dt} \tag{5.28}$$

From Eq. (5.24) written for $z = L$, both first and second moments can be theoretically obtained, and they are given by:

$$\bar{t} = \frac{L}{U}\left(1 + 2\frac{a}{LU}\right) \tag{5.29}$$

$$\sigma^2 = 2\left(\frac{L}{U}\right)^2 \frac{a}{LU}\left(1 + 4\frac{a}{LU}\right) \tag{5.30}$$

From these equations, the values of k and D_{12} are calculated:

$$k = \frac{2(2-\alpha)}{3+\sqrt{1+4\alpha}} \frac{u_0 \bar{t}}{L} - 1 \tag{5.31}$$

$$D_{12} = \frac{2\gamma}{\beta + \sqrt{\beta^2 - 4\gamma}} L u_0 \tag{5.32}$$

where

$$\alpha = \frac{\sigma^2}{\bar{t}^2} \tag{5.33}$$

$$\beta = \frac{2\alpha - 1 + \sqrt{1+4\alpha}}{4(2-\alpha)}$$

(5.34)

$$\gamma = \frac{1 + 6k + 11k^2}{(1+k)^2} \frac{R^2}{48L} \tag{5.35}$$

The moment method has been reported as less accurate than the curve fitting approach [29-30], but has been used to generate the first guesses of the parameters for the second one [37].

Funazukuri *et al*. [30] and Kong *et al.* [36-37] provide a detailed description of the CIR technique including the theoretical background, parameters sensitivity, and source of errors.

Nomenclature

a	Parameter defined by Eq. (5.25)
c	Solute concentration
C	Average cross section concentration (Eq. (5.9))
C_{app}	Average concentration of solute given by Eq. (5.14)
CIR	Chromatographic impulse response method
c_{p}	Specific heat of solution
CPB	Chromatographic peak broadening technique
D	Axial dispersion coefficient given by Eq. (5.11)
D_{12}	Tracer diffusion coefficient
De	Dean number, $\mathrm{De} = \mathrm{Re}\big/\sqrt{\zeta}$
h_{i} and h_{f}	Distances in geometric method
H	Theoretical plate height
k	Retention factor
L	Column length
m	Mass of injected solute
n	Refraction index
r	Radial coordinate
R	Inner radius of the dispersion tube
R_{c}	Coil radius
Re	Reynolds number, $\mathrm{Re} = 2\,R\,u_0\,\rho_1/\eta_1$
Sc	Schmidt number, $\mathrm{Sc} = \eta_1\,/(\rho_1 \cdot D_{12})$
t	Time
t_1 and t_2	Times at 10% peak height of the response curve ($t_1 < t_2$)
u_0	Average linear velocity of the solvent
$u_{0,\mathrm{opt}}$	Average linear velocity that minimizes H, $u_{0,\mathrm{opt}} = \sqrt{48}\,(D_{12}/R)$
U	Parameter defined by Eq. (5.26)
$W_{0.607}$	Half width at 60.7% of the peak height
Y^*	Solute solubility
z	Axial coordinate

Greek letters

α	Parameter defined by Eq. (5.33)
β	Parameter defined by Eq. (5.34)
γ	Parameter defined by Eq. (5.35)
$\delta\omega\left(r,t\right)$	Fluctuations in the local dielectric constant
ε	Root mean square error defined by Eq. (5.21)
ζ	Geometric factor, $\zeta = R_{\mathrm{c}}/R$
η_1	Solvent viscosity
θ	Scattering angle
λ	Thermal conductivity
λ_{rad}	Incident wavelength of the incident light under vacuum
ρ_1	Solvent density
σ^2	response curve variance
χ	Thermal diffusivity

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6. Experimental Set-up and D_{12} Measurements

In last decades, supercritical fluids (SCF) have been attracting widespread interest, especially the carbon dioxide (CO_2) utilization as supercritical solvent or reaction medium, due to its low critical temperature, moderate critical pressure, negligible surface tension, non-flammability, non-toxicity, etc. Hence, the experimental determination of binary diffusivities of different solutes in supercritical carbon dioxide (SC-CO_2) is very desired.

In this work, a new chromatograph was assembled to carry out measurements of diffusion coefficients, in liquid and supercritical fluids/mixtures. The diffusivities of acetone, toluene and eucalyptol in supercritical carbon dioxide (SC-CO_2) were obtained using the chromatographic peak broadening (CPB) technique.

Eucalyptol ($C_{10}H_{18}O$, Synonyms: 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane, 1,8-epoxy-*p*-menthane, cineole) is a cyclic ether and a very common monoterpenoid in essential oils of plants, especially in *Eucalyptus* where it can be present up to 90%. It has many different applications in distinct areas like food flavouring agent in treatments of airways diseases [1], in pharmaceutical industry, in drug formulations as a percutaneous penetration enhancers [2], in insect repellents, and it has been recognized to have antimicrobial activity [3], and anti-inflammatory activity in bronchial asthma [4].

Binary diffusion coefficients of terpenoids in SC-CO_2 are scarce, being available only for linalool [5], citral and D-limonene [6], α-pinene and β-pinene [7], L-menthone [8], L-carvone [8-9], and geraniol [9].

This chapter describes in detail the experimental set-up and procedures adopted for measuring tracer diffusivities in SC-CO_2.

6.1. Experimental Set-up and Procedure

An experimental set-up to measure tracer diffusion coefficients in liquid and supercritical fluids was designed and assembled. In Figure 6.1 some pictures of the apparatus installed are shown. It is essentially composed by:

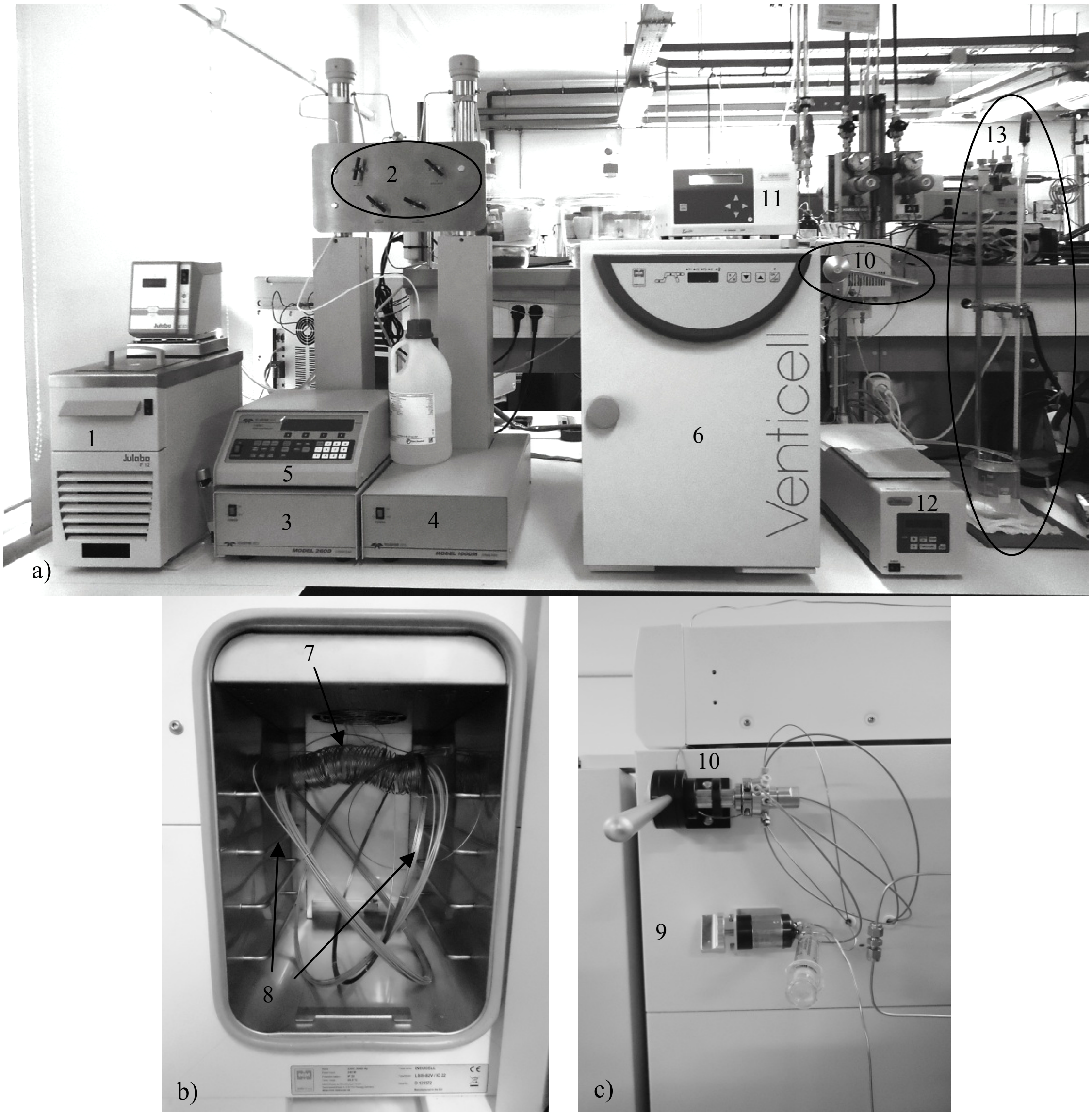

Figure 6.1. Experimental set-up for tracer diffusivity measurements in this work: 1) thermostatic bath, 2) inlet an outlet high pressure valves, 3) syringe pump for CO_2 or liquid solvent, 4) syringe pump for liquid (cosolvent); 5) syringe pumps controller; 6) oven; 7) pre-heating column; 8) diffusion columns; 9) injector; 10) high pressure selector; 11) UV detector; 12) BPR; and 13) soap bubble flow meter.

i) a thermostatic bath (F12, Julabo) used to control the temperature ($\pm 0.1\,\mathrm{K}$) of the CO_2 inside the solvent pump in order to keep a constant volumetric flow rate along experiments (see Figure 6.1a);

ii) two syringe pumps (260D and 100DM, Teledyne ISCO, with 266.05 mL and 102.93 mL, respectively) coupled with a controller unit to impose the volumetric flow rate of the solvents (Figure 6.1a). The fluctuations in the flow rates are $\pm 1.0\,\mu\mathrm{L}\cdot\mathrm{min}^{-1}$ and $\pm 0.01\,\mu\mathrm{L}\cdot\mathrm{min}^{-1}$, for the solvent and cosolvent pumps, respectively;

iii) four high pressure valves (15-11AF2, High Pressure Equipment Company – HiP) to control manually the solvent and cosolvent admission and exit from the syringe pumps (Figure 6.1a);

iv) an oven (LSIS-B2V/IC 22, Venticell, MMM Group) to fix the temperature of the diffusion columns during measurement. It possesses a fluctuation of $\pm 1\,\mathrm{K}$ (Figure 6.1a);

v) a preheating column (stainless steel tubing, 1/16'' O.D. × 10 m) placed inside the oven to preheat the mobile phase until the desired temperature (Figure 6.1b);

vi) an injector with an internal loop of 0.1 μL (C74H-1674-.1, Valco Instruments Co. Inc.) used to inject the pulse of solute to be analysed (Figure 6.1c);

vii) a manual high pressure selector (CSR4UW, Valco Instruments Co. Inc.) to choose the required diffusion column (Figures 6.1a and 6.1c);

viii) two diffusion columns of PEEK$^{\mathrm{TM}}$ (polyetheretherketone) with lengths $L = 20.695$ and 10.300 m, internal radius $R = 0.261$ mm, and coiled with $R_{\mathrm{c}} = 30$ cm (Figure 6.1b);

ix) UV Detector 2500, Knauer with an analytical flow cell (A4061, Knauer) at columns outlet (Figure 6.1a);

x) a back pressure regulator (BPR) (BP-2080 Plus, Jasco) to control the system pressure during the experiments (Figure 6.1a), equipped with a temperature controller.

xi) a soap bubble flow meter placed after the BPR, used to measure the solvent flow rate (Figure 6.1a).

The response of the system is monitored using a LabVIEW® program written specifically for this set-up, where the time and the absorbance for the wavelength selected are continually recorded and displayed graphically in the computer along runs. The data measured are saved into a spreadsheet file for further mathematical analysis. Since the two columns utilized are uncoated, the diffusion coefficients are obtained analysing the variance of the peaks by the CPB principles (Eqs. (5.19) – (5.20) or (5.21)), using program codes developed in Matlab 2009b® during this work.

In Figure 6.2 a schematic representation of the experimental apparatus to measure tracer diffusivities is shown. It can be divided in three distinct zones: *i*) admission of the solvent to the syringe pump and subsequent pressurization of the system, at constant volumetric flow rate, until reaching the desired pressure controlled by BPR; *ii*) solvent preheating, and solute injection into the diffusion column placed inside the oven at fixed temperature; and *iii*) solute detection by a UV detector.

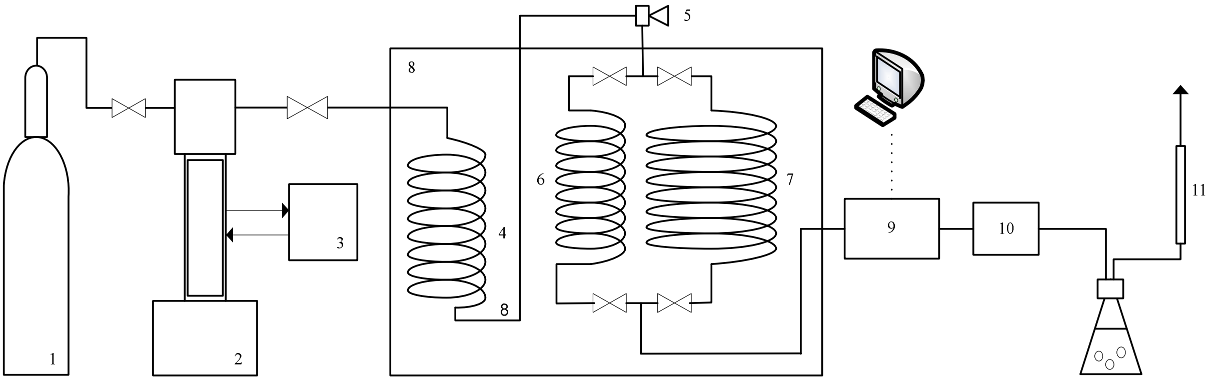

Figure 6.2. Schematic layout of the experimental apparatus for measure tracer diffusion coefficients. 1) CO_2 cylinder, 2) syringe pump, 3) thermostatic bath; 4) pre-heating column, 5) injector, 6) and 7) diffusion columns with different lengths, 8) oven, 9) UV detector, 10) BPR, and 11) soap bubble flow meter.

In this work, the D_{12} measurements were performed using supercritical carbon dioxide as solvent. The pure CO_2 from a cylinder at room temperature is admitted to the solvent syringe pump (266.05 mL), and it is fed to the preheating and diffusion columns (large and small) until the desired pressure is established by the BPR. From this point, the system is held under the assigned temperature, pressure and flow rate during 3 – 4 h prior to solute injection. The solute (liquid at room temperature) is loaded into the solvent stream using the injection valve, and the absorbance at column exit is monitored in the UV detector for a previously selected wavelength. Four to six pulses are injected into the system, spaced by 10 to 15 minutes intervals, in order to avoid any peaks overlap.

6.2. Equipment Tests

6.2.1. Chemicals

Solutes: Acetone (Sigma Aldrich, purity 99.8% w/w), eucalyptol (Sigma Aldrich, purity 99% w/w), ethanol (Fisher Chemical, purity 99.99% w/w), 2-propanol (Sigma Aldrich, purity 99.9% w/w), *n*-hexane (Fisher Scientific, purity 98.71% w/w), *n*-nonane (Sigma Aldrich, purity 99% w/w), and toluene (Sigma Aldrich, purity 99.9% w/w). Solvent: carbon dioxide (Praxair, purity 99.999% v/v).

6.2.2. Diffusivity Measurements

With the purpose to test the new set-up, some experiments were performed in order to detect peaks adsorption onto column walls, and verify the consistency of results and reproducibility.

The solute adsorption inside column wall originates tailored peaks, and, as observed by Feist and Schneider [10], such phenomenon becomes more noticeable for high molecular weight and polar compounds, especially in the low density region of the solvent. In order to check the inertness of the PEEK columns, the mean retention times (t_R) for several injections of acetone, ethanol, 2-propanol, *n*-hexane and *n*-nonane were measured at 313.15 K, 159 bar, and pump volumetric flow rate $\dot{Q}_{\text{pump}} = 0.13\,\text{mL}\cdot\text{min}^{-1}$, using the long column ($L = 20.695$ m). The results are listed in Table 6.1, being possible to observe that all retention times differ between them 42 s at most, which represents only 1.85% deviation, despite the distinct polarity, size and shape of the solutes. This confirms that there is no detectable adsorption onto the inner walls of this type of columns, and so they can be used with advantage over the conventional stainless steel ones.

Table 6.1. Residence time of different solutes for the long column at 313.15 K and 159 bar.

Solute	t_R (s)
acetone	2275
ethanol	2298
2-propanol	2256
n-hexane	2288
n-nonane	2265

The influence of initial dispersion of the solute during injection and the presence of dead volumes were analysed by measuring the solute diffusivities with the aid of the two PEEK columns ($L = 20.695$ and 10.300 m) and applying the subtraction technique to the variance of both peaks [11-12]:

$$H_{\mathrm{subt}} = \frac{\sigma^2_{\mathrm{long}}(t) - \sigma^2_{\mathrm{short}}(t)}{L_{\mathrm{long}} - L_{\mathrm{short}}} u_0^2 \qquad (6.1)$$

Thus, the resultant variance corresponds to that of a peak that would be produced in a column with an intermediate length ($L = 20.695 - 10.300 = 10.395$ m) where the above mentioned interferences are not present. The results obtained in this work for D_{12} measurements of acetone in SC-CO$_2$ using both columns, for two different operating conditions, show that the corrections found were inferior than 1.5%, which indicates that the undesired dispersion factors are negligible. A typical chromatogram for the acetone in SC-CO$_2$ obtained during the experiments is patent in Figure 6.3.

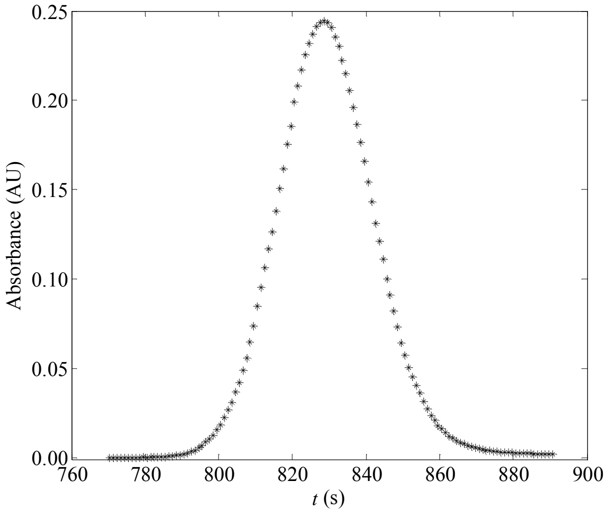

Figure 6.3. Example of an experimental response curve obtained in this work for acetone in SC-CO$_2$ ($T = 313.15$ K, $P = 150$ bar, $L = 10.300$ m, and 265 nm).

The reliability of the experimental unit and procedures adopted were evaluated by comparing the binary diffusivities of acetone and toluene in SC-CO_2 measured in this work ($T = 308.15$ and 313.15 K and $P = 150$ to 252 bar for acetone, and $T = 313.15$ to 333.15 K and $P = 202$ and 252 bar for toluene) with data available in literature from Sassiat *et al.* [13], Funazukuri *et al.* [14], Lai and Tan [15] and Suárez *et al.* [16]. Tables 6.2 and 6.3 compile our experimental diffusivities, and Figure 6.4 and 6.5 shows a comparison between them and data published. The measurements of acetone in SC-CO_2 were carried out for 265 nm in the UV detector [14], while for toluene they were determined for 260 nm.

Table 6.2. Experimental conditions and tracer diffusion coefficients of acetone in SC-CO_2.

T (K)	P (bar)	D_{12} ($10^{-4}\text{cm}^2\cdot\text{s}^{-1}$)
308.15	150	1.50
308.15	202	1.29
308.15	252	1.20
313.15	150	1.57
313.15	160	1.51
313.15	202	1.38
313.15	252	1.27

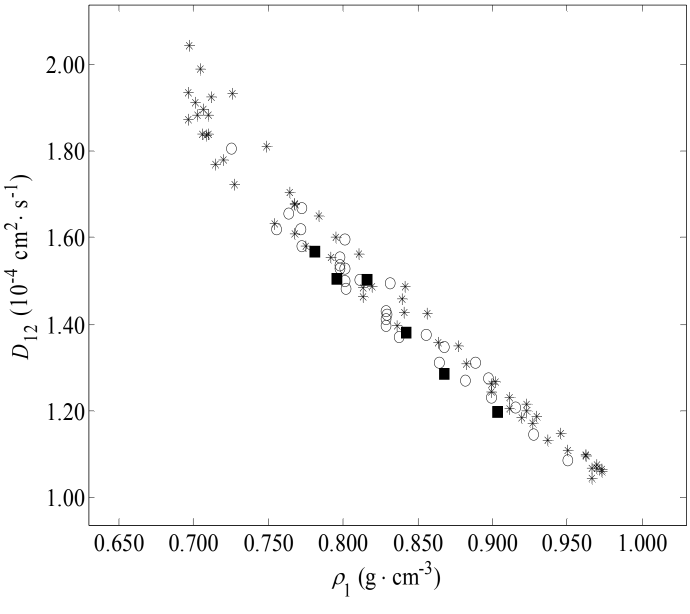

Figure 6.4. Comparison between (■) measured and reported ((○) Sassiat *et al.* [13] and (∗) Funazukuri *et al.* [14]) diffusion coefficients of acetone in SC-CO_2.

Table 6.3. Experimental conditions and binary diffusion coefficients of toluene in SC-CO$_2$.

T (K)	P (bar)	D_{12} (10^{-4}cm$^2\cdot$s^{-1})
313.15	202	1.18
313.15	252	1.06
323.15	202	1.28
323.15	252	1.13
333.15	202	1.40
333.15	252	1.26

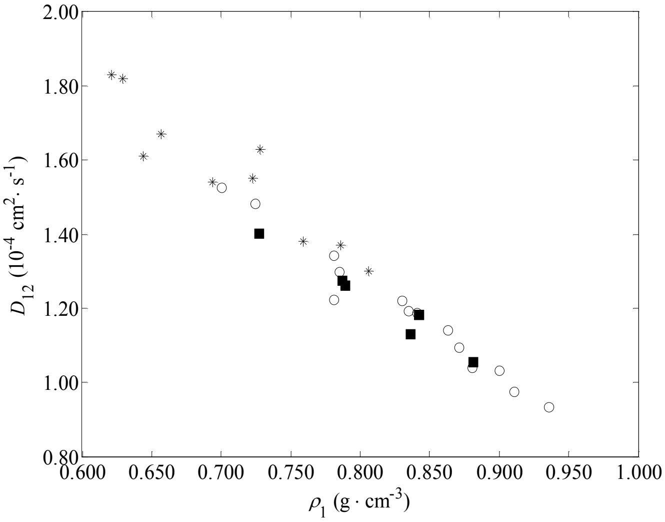

Figure 6.5. Comparison between (■) measured and reported ((○) Suárez *et al.* [16] and (∗) Lai and Tan [15]) tracer diffusion coefficients of toluene in SC-CO$_2$.

The good agreement found between D_{12} values measured and reported in literature, in both systems, validates the experimental procedure, equipment and mathematical approaches.

6.3. Measurements and Modelling of Tracer Diffusivities

Tracer diffusion coefficients of eucalyptol were measured in supercritical carbon dioxide in the range of $T = 313.15$ to 333.15 K, and $P = 202$ and 252 bar. The carbon dioxide was fed by the syringe pump at flow rate of 0.150 mL·min^{-1}. The linear velocity of CO$_2$ was determined with a soap bubble flow meter, and it was also estimated from the response curve. Solvent densities and viscosities were calculated by the correlations of

Pitzer and Schreiber [17], and Altunin and Sakhabetdinov [18], respectively. During experiments, the following conditions were observed:

i) laminar flow rate (Reynolds number, Re < 83);

ii) Gaussian concentration profiles, once the Levenspiel and Smith [19] criterion (see Eq. (5.16)) was verified in all cases, $D/(u_0 L) < 0.001$. In addition, all asymmetric factors, S_{10}, lie in the range 1.01 – 1.10;

iv) secondary flow effects inside the column were negligible, since values $\mathrm{De}\sqrt{\mathrm{Sc}} < 6.8$ (see criterion given by Eq. (5.17)).

The D_{12} data obtained for eucalyptol in supercritical carbon dioxide, together with the solvent densities and viscosities, are presented in Table 6.4. Each data point was determined by computing the variance of the response curves (Eqs. (5.19) and (5.20)), being the average of at least 3 – 4 injections. The experimental diffusivities, solvent density and viscosity ranged from 0.860×10^{-4} to 1.21×10^{-4} $\mathrm{cm^2{\cdot}s^{-1}}$, 0.7277 to 0.8594 $\mathrm{g{\cdot}cm^{-3}}$, and 0.0610 to 0.0835 cP, respectively.

Table 6.4. Experimental diffusivities of eucalyptol in carbon dioxide at different operating conditions.

T (K)	P (bar)	ρ_1 ($\mathrm{g{\cdot}cm^{-3}}$)	η_1 (cP)	D_{12} ($10^{-4}\mathrm{cm^2{\cdot}s^{-1}}$)
313.15	202	0.8425	0.0800	0.860
323.15	202	0.7876	0.0701	1.02
333.15	202	0.7277	0.0610	1.21
318.15	252	0.8594	0.0835	0.903
323.15	252	0.8366	0.0790	0.966
328.15	252	0.8132	0.0746	0.953
333.15	252	0.7893	0.0706	1.06

In the following, the influence of solvent density and viscosity upon D_{12} was examined, and the data were modelled using predictive and correlation models. The properties of eucalyptol necessary for the calculations are listed in Table 3.2.

In Figure 6.6 the diffusion coefficients of eucalyptol in supercritical carbon dioxide are plotted as a function of density at different pressure, as well as the calculated results obtained using three models developed in this work, namely the equation based on the Rice and Gray approach (Model 1: Eqs. (16) – (25), Paper II), the correlation with an exponential activation term to represent the attractive forces (Model 2: Eqs. (8) – (17), Paper III), and the free-volume model (Model 3: Eqs. (5) + (2) – (4), Paper V). The fitted parameters (if exist) and the average absolute relative deviations (AARDs) for all models derived and studied in this work are listed in Table 6.5. In Figure 6.6 it is possible to observe a huge dependence of eucalyptol diffusivities with carbon dioxide density. By increasing solvent density, the diffusion coefficient diminishes as a result of the decreasing free volume of the solvent and increasing intermolecular interactions [20-21]. In general, all models provide low or acceptable deviations to the experimental data (AARD = 2.26 – 57.68%), particularly those developed in this work (AARD = 2.26 – – 4.00%).

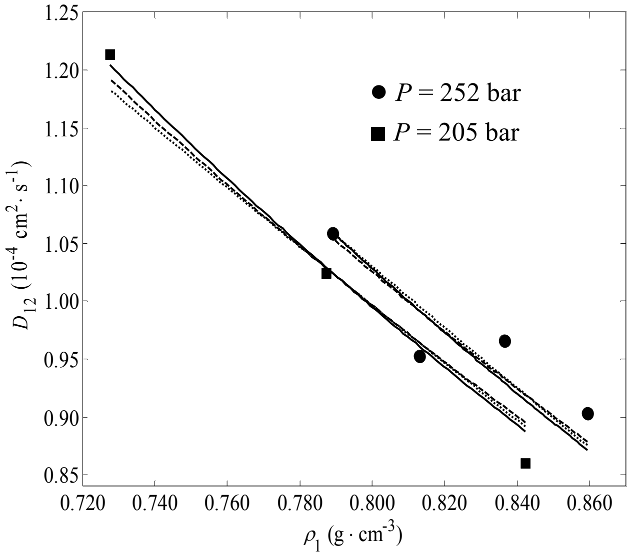

Figure 6.6. Binary diffusion coefficients of eucalyptol as a function of SC-CO_2 density. Modelling results: (—) Model 1 (Eqs. (16) – (25), Paper II), (- -) Model 2 (Eqs. (8) – (17) Paper III) and (···) Model 3 (Eq. (5) + Eqs. (2) – (4), Paper V) models.

Table 6.5. Parameters and global deviations found using all models developed and studied in this work.

Model	Equation	Nº of parameters	Parameters	AARD
Model 1	Eqs. (16) – (25), Paper II	1	$k_{12} = 0.09924$	2.26
Model 2	Eqs. (8) – (17), Paper III	1	$E_\mathrm{D} = 7.6910 \times 10^{9}\ \mathrm{erg \cdot mol^{-1}}$	2.41
Model 3	Eqs. (5) + (2) – (4), Paper V	1	$E_\mathrm{a} = 1.2105 \times 10^{10}\ \mathrm{erg \cdot mol^{-1}}$	2.48
Model 4	Eqs. (18) + (4) – (16), Paper VI	2	$\sigma_{\mathrm{LJ},1} = 3.54510\ \text{Å}$ $E_\mathrm{D} = 51.320\ \mathrm{J \cdot mol^{-1}}$	2.33
Model 5	Eq. (1), Paper VII	2	$a_1 = 1.9956 \times 10^{-8}\ \mathrm{cm^2 \cdot cP \cdot K^{-1} \cdot s^{-1}}$ $b_1 = 1.1308 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$	2.46
Model 6	Eq. (2), Paper VII	2	$a_2 = 1.9344 \times 10^{-8}\ \mathrm{cm^2 \cdot cP \cdot K^{-1} \cdot s^{-1}}$ $b_2 = 4.3173 \times 10^{-8}\ \mathrm{cm^2 \cdot K^{-1} \cdot s^{-1}}$	2.40
Model 7	Eq. (3), Paper VII	2	$a_3 = -0.8467$ $b_3 = -17.2087$	2.45
Model 8	Eq. (4), Paper VII	2	$a_4 = 0.8776$ $b_4 = -16.5815$	2.51
Model 9	Eq. (5), Paper VII	2	$a_5 = 7.5233 \times 10^{-6}\ \mathrm{cm^2 \cdot cP \cdot s^{-1}}$ $b_5 = -2.7956 \times 10^{-6}\ \mathrm{cm^2 \cdot s^{-1}}$	3.06
Model 10	Eq. (6), Paper VII	2	$a_6 = -1.0168$ $b_6 = -11.8697$	3.07
Model 11	Eq. (7), Paper VII	2	$a_7 = -6.4217 \times 10^{-7}\ \mathrm{cm^5 \cdot g^{-1} \cdot K^{-1} \cdot s^{-1}}$ $b_7 = 8.2561 \times 10^{-7}\ \mathrm{cm^2 \cdot K^{-1} \cdot s^{-1}}$	2.58
Model 12	Eq. (8), Paper VII	2	$a_8 = -5.1105 \times 10^{-7}\ \mathrm{cm^2 \cdot K^{-1} \cdot s^{-1}}$ $b_8 = 1.9710 \times 10^{-7}\ \mathrm{cm^2 \cdot K^{-1} \cdot s^{-1}}$	2.41
Model 13	Eq. (9), Paper VII	2	$a_9 = 4.2618 \times 10^{-8}\ \mathrm{cm^5 \cdot g^{-1} \cdot K^{-1} \cdot s^{-1}}$ $b_9 = 1.9982 \times 10^{-8}\ \mathrm{cm^2 \cdot cP \cdot K^{-1} \cdot s^{-1}}$	2.42
Model 14	Eqs. (2) + (13), Paper VIII	0	–	3.81
Model 15	Eqs. (13) + (2) – (5) , Paper VIII	0	–	4.00
TLSM	Eqs. (2.64) + (2.57) + (2.65)	0	–	18.60
TLSM$_\mathrm{d}$	Eqs. (1) + (7) – (11), Paper I	1	$k_{12,\mathrm{d}} = 0.10025$	2.33
Dymond	Eq. (2.87)	2	$B = 1.8234 \times 10^{-7}\ \mathrm{mol \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1/2}}$ $V_\mathrm{D} = 24.29\ \mathrm{cm^3 \cdot mol^{-1}}$	2.60
He-Yu-Su	Eqs. (2.88) – (2.90)	0	–	5.21
Zhu *et al.*	Eqs. (2.68) – (2.69) + (2.71) – – (2.74) + (2.83) – (2.84)	0	–	7.06
Wilke-Chang	Eq. (2.92)	0	–	8.12
Tyn-Calus	Eq. (2.94)	0	–	4.03
Scheibel	Eq. (2.95)	0	–	3.95
Reddy-Doraiswamy	Eqs. (2.96) and (2.97)	0	–	57.68
Lusis-Ratcliff	Eq. (2.98)	0	–	11.18
Lai-Tan	Eq. (2.99)	0	–	14.03

Figure 6.7 illustrates the eucalyptol diffusivities graphed in Stokes-Einstein coordinates, and the modelling results achieved by the *modified-Stokes-Einstein*-1 ($\mathrm{mSE_l}$, Eqs. (2) + (13), Paper VIII) and Wilke-Chang (Eq. (2.92), Chapter 2) predictive equations. As can be seen, the plot is approximately linear and the trend of results is consistent with those found by other authors [6, 13, 22-26]. From Figure 6.7 one can also verify that the $\mathrm{mSE_l}$ model accompanies more accurately the experimental data than the Wilke-Chang equation, and this is reinforced by the global deviations found for both predictive models: AARD ($\mathrm{mSE_l}$) = 3.81% and AARD (Wilke-Chang) = 8.12%.

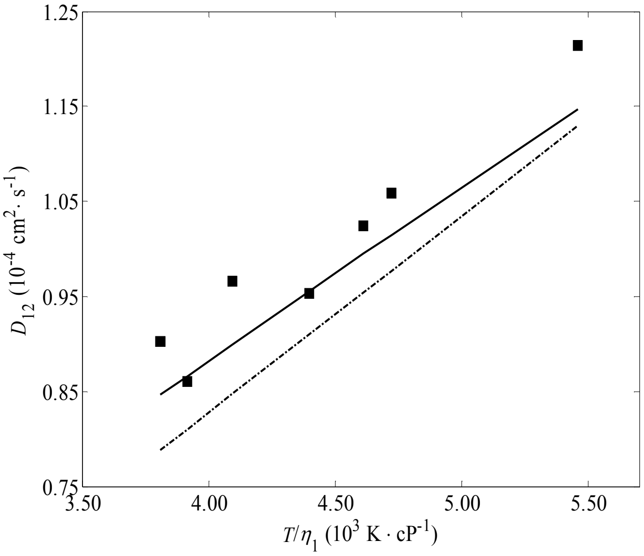

Figure 6.7. Experimental diffusion coefficients of eucalyptol plotted in Stokes-Einstein fashion along with modelling results: (—) $\mathrm{mSE_l}$ (prediction; this work) and (-·-) Wilke-Chang equations.

Nomenclature

AARD	Average absolute relative deviation
BPR	Back pressure regulator
CPB	Chromatographic peak broadening technique
D	Axial dispersion coefficient given by Eq. (5.11)
De	Dean number
D_{12}	Binary diffusion coefficient at infinite dilution
H	Theoretical plate height
L	Column length
P	Pressure
R	Inner radius of diffusion column
R_c	Coil radius
Re	Reynolds number
Sc	Schmidt number
SC-CO_2	Supercritical carbon dioxide
S_{10}	Asymmetric factor given by the ratio of the latter half to the front width at 10 % peak height
T	Temperature
t_R	Retention time
u_0	Average linear velocity of the solvent

Greek Letters

η_1	Solvent viscosity
ρ_1	Solvent density
σ^2	Peak variance

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7. Conclusions

The main conclusions of this work are presented in the following, separated in three distinct groups: tracer diffusion coefficients of hard sphere fluid; binary diffusion coefficients of real fluids, including the database collected; experimental set-up and measurement of binary diffusivities.

(1) A new accurate expression for tracer diffusion coefficients of hard spheres, more specifically the hard sphere correction factor F_{12} (Eq. (23) + Eqs. (24) and (25), Paper I), was proposed and validated using molecular dynamics data taken from literature. The results are much better than those achieved by other well known and established models: $\mathrm{AARD} = 4.44\%$ (this work) against deviations between 18.20% and 67.78% (Sung and Stell, Eaton and Akgerman, Easteal and Woolf, and Sun and Chen expressions).

(2) With relation to binary diffusion coefficients of real systems, a database was collected and a set of models was developed according to different theoretical approaches.

The largest database of tracer diffusivities in liquid, gas, and supercritical solvents was compiled and used to validate the new models derived. It comprehends 622 binary systems totalizing 9407 data points and involving 358 molecules. The solvents are non-polar, weakly-polar and polar.

Concerning the new models, it was observed that systems where solvent is non-polar or weakly-polar, 1-parameter correlations are sufficient to interpret the diffusion phenomenon accurately over wide ranges of temperature and density, while for polar systems two parameters are required.

– Comparing the models specific for non-polar and weakly-polar solvents, the $\mathrm{TLSM_d}$ expression (Eqs. (1) + (7) – (11), Paper I), with interaction parameter $k_{12,\mathrm{d}}$ in the diameter combining rule, is recommended for calculations ($\mathrm{AARD} = 3.89\%$). The new models published in Paper II (Eqs. (16) – (25)) and Paper III (Eqs. (8) – (17)) also provide reliable representations of experimental data (AARDs between 4.26% and 4.44%).

– For any solvents, polar and non-polar, it is recommended the 2-parameter Lennard-Jones model given by Eqs. (18) + (4) – (16)) (Paper VI); the required parameters are the solvent molecular diameter, $\sigma_{1,\mathrm{LJ}}$, and the diffusion activation energy, E_D.

– Diffusivities of systems with polar solvents may be alternatively estimated by the very simple empirical expression relating D_{12} with temperature and solvent viscosity (Eq. (3), Paper VII). Despite possessing two parameters per system, it was shown that two data points are sufficient to optimize them and ensure simultaneously reliable interpolation and extrapolation ability for D_{12} calculation.

– For the particular case of supercritical carbon dioxide and liquid water as solvents, the hybrid free-volume correlation developed in Paper V (Eqs. (5) + (2) – (4)), includes one parameter (activation energy, E_a) and can be used successfully to estimate D_{12}. In this model, the unique solute property necessary for the calculations is the molecular weight. The average errors are 3.39% and 4.18% for SC-CO_2 and liquid water, respectively.

– When experimental diffusion coefficients in supercritical carbon dioxide are unavailable, their prediction can be carried out using the modified *Stokes-Einstein*-1 expression proposed in Paper VIII (Eqs. (2) + (13)), for which the average deviation is 6.38%.

(3) An experimental set-up to measure tracer diffusion coefficients in liquid and supercritical fluids and mixtures was designed and assembled. Equipment tests were carried out by measuring tracer diffusion coefficients of acetone and toluene in SC-CO_2 for which there are many data published. A good agreement was found for both systems studied. Furthermore, diffusivities of eucalyptol in supercritical carbon dioxide were measured by the chromatographic peak broadening method, between 202 bar and 252 bar, and 313.15 K and 333.15K. The experimental diffusivities obtained are in the range of 0.860×10^{-4} to $1.21\times10^{-4}\ \mathrm{cm^2\cdot s^{-1}}$. The points were modelled using the expressions

developed in this thesis. A good agreement was obtained between experimental and calculated data, with errors between 2.26 and 4.00%.