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Rationalizing the use of mutual diffusion prediction models in non-ideal binary mixtures

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ABSTRACT

In this paper, we compared seven diffusion models in terms of prediction performances. Using vapour-liquid equilibrium (VLE) data, we calculate the thermodynamic correction factor as a function of composition for eleven binary liquid mixtures using non-random two-liquid and Redlich-Kister models. These data, together with intra-diffusion coefficients, and viscosity values, are used to predict mutual diffusivity.

The Darken-based models, which consider a scaling power on the thermodynamic factor, give accurate predictions, with absolute average relative deviation (AARD) values between 1 and 20 %. The removal of the scaling power leads to a decrease in prediction accuracy. The viscosity-based models with (*Vis-SF*) and without (*Vis-nSF*) scaling factor have AARD of 14 and 30 %, respectively. The dimerization model is inaccurate for most mixtures except those containing water, while the Vignes-based model (*V-Gex*), which is based on the Gibbs free energy, gave high AARD values of 25 %, hence, not as reliable when compared to the other models.

1. Introduction

Separation processes such as extraction, absorption, and distillation are heavily influenced by diffusion in liquids. Indeed, diffusion is a key mass transfer phenomenon and is of great importance in many areas of science and technology, including many unit operations in chemical engineering. There are different methods to design and control these unit operations. These include the equilibrium stage methods, rate-based methods, and the non-equilibrium methods (Guevara-Carrion et al., 2016).

The equilibrium-based methods are mostly used in modelling and design of these operations; however, they often yield a solution that differs from the real physical process, hence are often corrected by an empirical efficiency factor (Taylor & Krishna, 1993). The rate-based models are often used to solve simulation and modelling problems for both steady and unsteady state processes (Kenig & Blagov, 2014). Conversely, the non-equilibrium methods employ the use of mass and energy transfer models utilizing diffusion data, and other transport properties such as thermal conductivities and viscosities of the different systems under investigation. It is worth noting that both rate-based and non-equilibrium methods yield solutions that are much closer to physical reality. Therefore, there is a growing interest for accurate prediction of diffusion and, in general, transport properties and time-independent measurements such as vapour-liquid equilibrium (VLE) data, most especially in systems with challenging thermodynamic conditions, such as high degree of non-ideality.

The prediction of mutual diffusion coefficients, also referred to as inter-diffusion coefficients, described by Fick's law, is of great interest as this transport coefficient determines the rate of transport in many unit operations, such as extraction (Tudose & Apreotesei, 2001), adsorption (Staszak, 2016) and reaction (Terazima, 2006). Indeed, experimental measurements of mutual diffusion are quite challenging and lengthy and often require a complex experimental set up, such as for methods based on Taylor dispersion (D'Errico et al., 2004), holographic interferometry (Sanchez & Clifton, 1978) and light scattering (McKeigue & Gulari, 1984). Hence, prediction models can be valid alternatives for a rapid estimate of mutual diffusion coefficients. These models are very useful, for example they can help in prediction of transport properties in hazardous systems, which are difficult to investigate experimentally due to, for example, safety concerns.

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Whilst several models exist to predict diffusion of gaseous mixtures (Boudin et al., 2013; Hirschfelder et al., 1949), mutual diffusion in liquid systems, particularly non-ideal mixtures, is difficult to predict from first principles. For binary liquid mixtures, several prediction models based on the Darken and Vignes equations have been developed (Guevara-Carrion et al., 2016). These models are mostly based on the Maxwell-Stefan (MS) approach in which the mutual diffusion for a binary mixture is expressed as Eq. (1) (Allie-Ebrahim et al., 2018):

$$D_{12} = Ð_{12}\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right] \tag{1}$$

where $Ð_{12}$ is the MS diffusivity and the term in square brackets is the thermodynamic factor G, which accounts for non-idealities within the mixture caused by either repulsive or attractive interactions between species. The MS diffusivity cannot be directly measured; however, several semi-empirical correlations exist for obtaining this value, including those based on Vignes (Vignes, 1966) and Darken (Liu et al., 2011) models. For a binary mixture, the MS diffusivity based on the Darken equation, is written in Eq. (2) as:

$$D_{12} = D_1^* x_2 + D_2^* x_1 \tag{2}$$

where D_1^* and D_2^* are the self-diffusion coefficients (also referred to as tracer or intra-diffusion coefficients) of the single species in the mixtures measured at compositions x_1 and x_2, respectively. Thus, substituting Eq. (2) into Eq. (1):

$$D_{12} = \left(D_1^* x_2 + D_2^* x_1\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right] \tag{3}$$

Recent experimental work has shown that the use of a scaling power on the thermodynamic factor, which can be derived from scaling laws theory, improves significantly predictions of mutual diffusion (Zhao & Snurr, 2009). Previous work has also shown that in some cases, models accounting for dimerization of species within the mixture are more appropriate (D'Agostino et al., 2012; Moggridge, 2012a); models based on local composition have also been shown to give good predictions (Zhu, 2015 and Liu, 2011). For some mixtures, it has been shown that models based on the knowledge of viscosity (Zhu et al., 2016) and self-diffusion coefficients (D'Agostino et al., 2011) also give reasonably accurate mutual diffusivity predictions.

Whilst models for predicting mutual diffusion are clearly valid alternative tools to lengthy experimental measurements, there is still a general concern about the applicability of these models over a range of different mixtures depending on the chemical nature of the diffusing species, the type of bonding interactions involved, as well as the forces of attraction or repulsion within the mixtures. Nonetheless, a comprehensive comparison of these different prediction models is not well documented.

In this paper, we used several prediction models based on both Vignes and Darken equations and we test their prediction performance at 298.15 K. We chose eleven binary mixtures, including mixture of hydrocarbons, aromatics, water and alcohols. The choice of these studied systems are informed by the availability of experimental mobility data (e.g., availability of self-diffusion coefficients) as well as thermodynamic data. Indeed, it is not always trivial to find systems for which both diffusion and VLE data are both available, and at the same temperature. For the eleven mixtures chosen here both data sets are available, hence the analysis can be carried out. Also, the selection of the mixtures is driven by the need to investigate the effect of molecular interactions, such as hydrogen bonding and dimerization effects within these mixtures. To achieve our aim, we performed thermodynamic modelling of VLE data to calculate the thermodynamic factors and the Gibbs free energy. The mobility and thermodynamic data are then used together for testing the various models and predicting mutual diffusion coefficients. Mutual diffusion coefficients of binary fluid mixtures are generally predicted using mutual diffusion coefficients at infinite

Table 1
Binary mixtures analyzed in this work.

Component 1	Component 2
Benzene	Cyclohexane
Acetone	Cyclohexane
Ethanol	Water
Methanol	Ethanol
Benzene	Acetone
Cyclohexane	Ethanol
Ethanol	Benzene
n-Hexane	Toluene
Cyclohexane	Toluene
Acetonitrile	Water
Methanol	Benzene

Table 2
The seven different models used in this work and their abbreviations.

Model	Author	Abbreviation
Local volume fraction composition model	(Li et al., 2001)	*LV*
Darken-based model with scaling factor	(D'Agostino et al., 2011)	*D-SF*
Dimerization model with scaling factor	(D'Agostino et al., 2012)	*Dim-SF*
Local mole composition with scaling factor	(Zhu et al., 2015)	*LM-SF*
Vignes model based on Erying's theory and Gibbs energy	(Bosse & Bart, 2006)	*V-Gex*
Viscosity-based model with scaling factor	(Zhu et al., 2016)	*Vis-SF*
Viscosity-based model with no scaling factor	(Carman, 1967)	*Vis-nSF*

dilution or self-diffusion coefficients as a function of composition (depending on the choice of the model), or using viscosities of pure components and mixtures (Schlögl, 1985). It must however be noted that, within the regime of infinite dilution, the mutual diffusion coefficient is equal to the self-diffusion coefficient of the dilute species in the mixture. The predicted mutual diffusion coefficients of the studied systems are then compared with experimental values. A comprehensive comparison and a discussion correlating the applicability of the different models with the nature of the binary mixture is then carried out.

2. Materials and methods

This work examines seven different models for the prediction of the mutual diffusion coefficient of binary liquid-phase mixtures at 298.15 K. These models are proposed by Bosse and Bart (Bosse & Bart, 2006), Carman and Stein (Carman & Stein, 1956), (Li et al., 2001), (D'Agostino et al., 2011), (D'Agostino et al., 2012), (Zhu et al., 2015), and (Zhu et al., 2016). The models will be used to predict the mutual diffusion coefficients of eleven binary mixtures, which are highlighted in Table 1.

2.1. Diffusion models

The seven different models used in this study and their acronyms are shown in Table 2 and each model discussed in detail in subsequent sections.

2.1.1. Local volume composition model (LV)

The model proposed by Li et al. (Li et al., 2001) is based on the idea of local composition. By addressing cluster formation (Cussler & Cussler, 2009), an expression for the computation of concentration-dependent self-diffusion coefficients is constructed. In this case, an analogy is considered between non-ideal solutions and solutions that are near the consolute point, whereby the diffusion is modelled as a movement of clusters of molecules (Cullinan Jr, 1985). The mutual diffusion coefficient is predicted using Eq. (4):

$$D_{12} = \left(\frac{\phi_2 V}{V_2}D_1^* + \frac{\phi_1 V}{V_1}D_2^*\right)\left(1 + \frac{d\ln\gamma_2}{d\ln x_2}\right) \tag{4}$$

where γ_2 is the activity coefficient for component 2, V_i denotes the partial molar volume of the component i in the mixture, ϕ_i is the volume fraction of component i in the mixture, and D_i^* is the self-diffusion coefficient of component i in the mixture. The molar volume of the mixture V and the volume fractions, ϕ_1 and ϕ_2, are defined according to:

$$V = x_1 V_1 + x_2 V_2 \tag{5}$$

$$\phi_1 = \frac{x_1}{x_1 + x_2 G_{12}}, \phi_2 = \frac{x_2}{x_2 + x_1 G_{21}} \tag{6}$$

where G_{12} and G_{21} are model interaction parameters, which are derived from the VLE activity coefficient data modelling, and are computed by minimizing the objective functions of the thermodynamic model using the least squares method.

It is worth noting that the partial molar volume V_i in Eq. (4) is assumed to be the corresponding molar volume of the pure component i since there is a negligible difference between both values according to Li et al.(Li et al., 2001).

2.1.2. Darken-based model with scaling factor (D-SF)

This model is used to predict mutual diffusion coefficient from self-diffusion data obtained from pulsed field gradient nuclear magnetic resonance (PFG-NMR) measurements (Tanner, 1970) and a thermodynamic correction factor (D'Agostino et al., 2011). The expression for the mutual diffusion coefficient D_{12} is given as:

$$D_{12} = \left(x_1 D_2^* + x_2 D_1^*\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^\alpha \tag{7}$$

where γ_1 is the activity coefficient for component 1, and α is the thermodynamic correction factor.

This model is based on two assumptions:

i. The Darken theory, which originated from Fick's law of diffusion describing the concentration gradient as the driving force for diffusion, and thereafter assumes that the chemical diffusion of a binary liquid system is related to the atomic fractions of the two diffusing species;

ii. Semi-empirical scaling laws (Jany, 1990) associated with the critical point phenomena as a result of fluctuations in dynamic concentration.

2.1.3. Dimerization model with scaling factor (Dim-SF)

This model assumes that one of the species in the liquid mixture exhibits strong association and dimerizes (D'Agostino et al., 2012). Whilst a dimerized species can be expected to have a lower self-diffusivity than the eqivalent monomer (because its molecular weight is doubled), for each dimer which is displaced, two monomers have moved. As a result, the mass transfer of the species experiencing dimerization is twice in value to the measured self-diffusivity. This is because for every labelled molecule that moves, a second unlabelled molecule will also move (Carman, 1967). Thus, for a binary liquid mixture, Eq. (7) is modified to give the mutual diffusion coefficient in which one of the components is strongly dimerized as:

$$D_{12} = \left(2x_1 D_2^* + x_2 D_1^*\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^\alpha \tag{8}$$

2.1.4. Local mole composition with scaling factor (LM-SF)

This model predicts the mutual diffusion coefficient using the concept of local mole fraction obtained from the NRTL (non-random two-liquid) model, as well as scaling law effects for the thermodynamic correction factor (Zhu et al., 2015). It assumes that diffusion occurs as a

result of strong molecular association resulting in a highly correlated movement. Hence, no prior knowledge of the extent of molecular association is required in predicting the mutual diffusion coefficient from self-diffusion coefficient.

The mutual diffusion coefficient is evaluated using:

$$D_{12} = \left(x_{11}D_2^* + x_{22}D_1^*\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^\alpha \tag{9}$$

The local molar fractions of the components in the mixture x_{11} and x_{22} explain the effect of intermolecular association (molecular mobility), whilst keeping the scalar power α of the thermodynamic factor constant.

2.1.5. Vignes model based on Erying's theory and Gibbs energy (V-Gex)

This is a Vignes-based model where diffusion coefficient determination relies on Eyring's theory of absolute rate of reaction (Bosse & Bart, 2006). For binary systems, the MS diffusivity equals the ideal diffusivity, which is a function of the reaction rate constant k and distance between two equilibrium positions λ. The rate constant is dependent on the equilibrium constant, which relates the diffusing molecules in both standard and activated states and can be expressed in terms of net energy of activation of the diffusion process called the Gibbs energy ΔG_{ij}.

The diffusivity at infinite dilution D_{ij}^∞ is expressed as:

$$D_{ij}^\infty = \frac{\lambda^2 k_B T}{h}\exp\left(-\frac{\Delta G_{ij}^\infty}{RT}\right) \tag{10}$$

where h and k_B are the Planck and Boltzmann constants, R is the universal gas constant, while ∞ represents infinite dilution conditions.

For ideal systems, a linear relationship of the net activation energy is assumed and is expressed as:

$$\Delta G_{ij} = x_j \Delta G_{ij}^\infty + x_i \Delta G_{ji}^\infty \tag{11}$$

However, for non-ideal mixtures with small diffusivity values (Bosse & Bart, 2006), the mixing rule (Cullinan Jr, 1966) is employed to give:

$$\Delta G_{ij} = x_j \Delta G_{ij}^\infty + x_i \Delta G_{ji}^\infty + G^{ex} \tag{12}$$

Thus, the mutual diffusion coefficient is expressed as a function of infinite dilution and excess Gibbs energy G^{ex}.

$$D_{ij} = (D_{ij}^\infty)^{x_j}\left((D_{ji}^\infty)^{x_i}\right)\left(-\frac{G^{ex}}{RT}\right) \tag{13}$$

2.1.6. Viscosity-based model with scaling factor (Vis-SF)

This model predicts the mutual diffusion coefficients over the entire composition range for binary systems containing one self-associating species and one non-polar species (Zhu et al., 2016). It is based on the Darken theory, which considers the cluster diffusion approach and a scaling power of the thermodynamic factor, while using the viscosity data and self-diffusion coefficients at infinite dilution of both components.

The mutual diffusion coefficient of binary liquid system for this model is obtained from the modification of the Darken's equation and is written as:

$$D_{12} = \frac{1}{\eta}\left(x_1\eta_1 D_{21}^\infty + x_2\eta_2 D_{12}^\infty\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right]^\alpha \tag{14}$$

where D_{ij}^∞ represents the mutual diffusion coefficient in the binary mixture of component i infinitely diluted in component j, η_i denotes the viscosity of component i in pure liquid, η is the viscosity of the mixture, and α is the scaling factor taken as 0.64 (Moggridge, 2012b).

2.1.7. Viscosity-based model without scaling factor (Vis-nSF)

This model is based on the same principle as the Zhu et al. (2016) model. The only difference is the removal of the thermodynamic scaling factor from the thermodynamic term. Hence, mutual diffusivity for this

model is expressed as:

$$D_{12} = \frac{1}{\eta}\left(x_1\eta_1 D_{21}^{\infty} + x_2\eta_2 D_{12}^{\infty}\right)\left[1 + \frac{d\ln\gamma_1}{d\ln x_1}\right] \tag{15}$$

2.2. Thermodynamic modelling

In this work, two thermodynamic models are employed to model the VLE data obtained from literature. These include the three-parameter NRTL model and four parameter Redlich-Kister model. The thermodynamic modelling involves the construction of an activity coefficient model by fitting the vapour pressure of the liquid mixtures, at a given temperature, into the expression:

$$P = x_1\gamma_1 P_1^{\text{SAT}} + x_2\gamma_2 P_2^{\text{SAT}} \tag{16}$$

where P is the total vapour pressure of the liquid mixture (Pa), x_i, γ_i and P_i^{SAT} represents the mole fraction, activity coefficient, and saturated vapour pressure of component i.

Eq. (16) assumes an ideal vapor phase, which neglects the Poynting correction (Sander et al., 1986).

The choice of two models is to serve as a check on either model to ensure the accuracy of our results. The thermodynamic correction factor reflects the thermodynamic non-idealities of the system and for pure components the value is 1. The parameter estimates of the models obtained are further used to determine the local mole fractions (in the case of NRTL), the excess Gibbs energy, and the thermodynamic factors. The VLE data for the studied mixtures are in the Supplementary Information (Table S1a-d).

2.2.1. NRTL thermodynamic model

The NRTL equation is a semi-empirical three-parameter equation based on the concept of local concentration and is used to derive the properties of multi-element gas–liquid equilibria and solution equilibria from binary data. It can be used for partially miscible systems and is therefore particularly suitable for the calculation of non-ideal liquid-liquid mixtures.

This relation (Wisniak, 1993):

$$\frac{G^{\text{ex}}}{RT} = F(x)G(x) \tag{17}$$

where $F(x) = x_1 x_2$ and $G(x) = \left[\frac{\tau_{21}G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1 G_{12}}\right] \tag{18}$

$$\frac{dG^{ex}}{dx_1} = F(x_1)G'(x_1) + G(x_1)F'(x_1) \tag{19}$$

$$\frac{d^2 G^{\text{ex}}}{dx_1^2} = F(x_1)G''(x_1) + 2F'(x_1)G'(x_1) + G(x_1)F''(x_1) \tag{20}$$

where $F'(x_1) = 1 - 2x_1$, and $F''(x_1) = -2 \tag{21}$

$$G'(x_1) = -\left[\frac{\tau_{21}G_{21}(1 - G_{21})}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12}G_{12}(G_{12} - 1)}{(x_2 + x_1 G_{12})^2}\right] \tag{22}$$

$$G''(x_1) = 2\left[\frac{\tau_{21}G_{21}(1 - G_{21})^2}{(x_1 + x_2 G_{21})^3} + \frac{\tau_{12}G_{12}(G_{12} - 1)^2}{(x_2 + x_1 G_{12})^3}\right] \tag{23}$$

where τ_{12} and τ_{21} are the interaction parameters, which are dimensionless and related to the energy interaction parameters $g_{12} - g_{21}$ and $g_{21} - g_{12}$ using the expression:

$$\tau_{12} = \frac{g_{12} - g_{21}}{RT}, \tau_{21} = \frac{g_{21} - g_{12}}{RT} \tag{24}$$

The local mole fractions x_{11} and x_{22} are obtained using the two interaction parameters G_{12} and G_{21}, according to:

$$x_{11} = \frac{x_1}{x_1 + x_2 G_{21}}, x_{22} = \frac{x_2}{x_2 + x_1 G_{12}} \tag{25}$$

Given that:

$$G_{12} = \exp(-\varepsilon_{12}\tau_{12}), G_{21} = \exp(-\varepsilon_{12}\tau_{21}) \tag{26}$$

ε_{12} is defined as the non-randomness term and is dependent on the nature of the pure components with values ranging from 0.2 to 0.5. Higher values represent higher non-randomness of the mixture (Zhu et al., 2015). The values of ε_{12} is taken as 0.3 for complete intercalation, $\varepsilon_{12} = 0.2$ for partial intercalation and, if required, a range of values from 0.2 to 0.5 for most intercalation systems (Renon & Prausnitz, 1968). In this work ε_{12} was set as 0.3 for the studied non-ideal systems and the interaction parameters were obtained by fitting the model to the VLE data.

2.2.2. Redlich-Kister (R-K) thermodynamic model

The four parameter Redlich-Kister expansion used in the determination of the excess Gibbs energy G^{ex} (Sandler, 2006). Eq. (17) is expressed as:

$$\frac{G^{ex}}{RT} = x_1 x_2\left\{A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3\right\} \tag{27}$$

where

$$x_2 = 1 - x_1 \tag{28}$$

$$F(x) = x_1 x_2 \tag{29}$$

$$G(x) = \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3\right] \tag{30}$$

The parameters A, B, C and D are obtained by performing a least square fit to the VLE data.

The chemical potential of a binary mixture written in the form of activity coefficient γ is expressed as:

$$\mu_1 = \mu_1^0 + RT\ln a_1 = \mu_1^0 + RT\ln(x_1\gamma_1) = \mu_1^0 + RT\ln x_1 + RT\ln\gamma_1 \tag{31}$$

where:

$$RT\ln\gamma_1 = F(x_1)G(x_1) + x_2[(F(x_1)G'(x_1) + G(x_1)F'(x_1)] \tag{32}$$

$$RT\ln\gamma_2 = F(x_1)G(x_1) - x_1[(F(x_1)G'(x_1) + G(x_1)F'(x_1)] \tag{33}$$

At constant temperature and pressure, the Gibbs-Duhem Equation for binary mixtures is expressed as (Smith et al., 1996):

$$x_1\frac{d\ln\gamma_1}{dx_1} = -x_2\frac{d\ln\gamma_2}{dx_1} \tag{34}$$

Rearranging the first term of Eq. (34) gives:

$$x_1\frac{d\ln\gamma_1}{dx_1} = \frac{d\ln\gamma_1}{d\ln x_1} \tag{35}$$

Thus, the thermodynamic factor is obtained by combining Eqs. (34) and (35):

$$1 + \frac{d\ln\gamma_1}{d\ln x_1} = 1 - \frac{x_2}{RT}\frac{d\ln\gamma_2}{dx_1} \tag{36}$$

Rearranging gives:

$$1 + \frac{d\ln\gamma_1}{d\ln x_1} = 1 - \frac{x_2}{RT}\frac{d}{dx_1}[\ln\gamma_2] \tag{37}$$

Also, differentiating Eq. (33) with respect to x_1 gives:

$$\frac{d\ln\gamma_2}{dx_1} = -x_1[F(x_1)G''(x_1) + 2F'(x_1)G'(x_1) + G(x_1)F''(x_1)] \tag{38}$$

Table 3
Table showing diffusion, viscosity, and VLE data at 298.15 K.

Comp. 1	Comp. 2	D_i(reference)	D_{ij} method of measurement/simulation (reference)	η(reference)	VLE Data (reference)
Benzene	Cyclohexane	(Aoyagi & Albright, 1972)	Diaphragm cell technique (Sanni et al., 1971; Sanni & Hutchison, 1973)	(Aoyagi & Albright, 1972)	(Tasić et al., 1978)
Ethanol	Water	(Zhang & Yang, 2005)	Molecular dynamics (Zhang & Yang, 2005)	(Dunstan & Thole, 1909)	(d'Avila & Silva, 1970; Faghihi et al., 2020; Phutela et al., 1979)
Acetone	Cyclohexane	(Puri et al., 1974)	Diaphragm cell technique (Bosse & Bart, 2006; Tasic et al., 1981)	(González et al., 2005)	(Puri et al., 1974) (Tasić et al., 1978)
Methanol	Ethanol	(Johnson & Babb, 1956; Par et al., 2013)	Taylor dispersion method, molecular simulation (Par et al., 2013)	(Canosa et al., 1998)	(Kooner & Fenby, 1980)
Cyclohexane	Ethanol	(Bosse & Bart, 2005)	Taylor dispersion method (Bosse & Bart, 2005)	(Papaioannou et al., 1991)	(Washburn & Handorf, 1935)
Acetonitrile	Water	(Easteal et al., 1987)	Diaphragm cell technique (Easteal et al., 1987)	(Cunningham et al., 1967)	(Treiner et al., 1976)
Benzene	Acetone	(Guevara-Carrion et al., 2016)	Molecular dynamics simulations (Guevara-Carrion et al., 2016)	(Howard & Pike, 1959; Petrino et al., 1995)	(Tasić et al., 1978)
Cyclohexane	Toluene	(Merzliak et al., 2006)	Diaphragm cell technique (Sanni et al., 1971; Sanni & Hutchison, 1973)	(Iloukhani et al., 2005)	(Katayama et al., 1965)
Ethanol	Benzene	(Guevara-Carrion et al., 2016; Johnson & Babb, 1956)	Optical diffusiometry, Predictive modelling (Anderson et al., 1958; Bosse & Bart, 2006)	(Dunstan, 1904)	(Hwang & Robinson Jr, 1977; Smith & Robinson Jr, 1970)
Methanol	Benzene	(Guevara-Carrion et al., 2016)	Molecular dynamics simulations (Guevara-Carrion et al., 2016)	(Guevara-Carrion et al., 2016; Han et al., 2006)	(Goral et al., 2004; Hwang & Robinson Jr, 1977; Miyano & Hayduk, 1993)
n-Hexane	Toluene	(Ghai & Dullien, 1974)	Diaphragm cell technique (Ghai & Dullien, 1974)	(Iloukhani et al., 2005)	(Funk & Prausnitz, 1970)

D_i represents the self-diffusion coefficient of component *i*.
D_{ij} represents the mutual diffusion coefficient of the mixture.

Thus, Eq. (37) becomes:

$$1 + \frac{d\ln\gamma_1}{d\ln x_1} = 1 + \frac{x_1 x_2}{RT}\left[F(x_1)G''(x_1) + 2F'(x_1)G'(x_1) + G(x_1)F''(x_1)\right] \quad (39)$$

The terms in the square bracket of Eq. (38) are the same as the right-hand side of Eq. (20). Eq. (39) can therefore be written as:

$$1 + \frac{d\ln\gamma_1}{d\ln x_1} = 1 + \frac{x_1 x_2}{RT}\frac{d^2 G^{ex}}{dx_1^2} \quad (40)$$

Eq. (40) is the thermodynamic factor, which is applicable for both NRTL and Redlich-Kister models.

In order to obtain a good Redlich-Kister fit, Eqs. (27) and (30) can be reduced to a one-parameter, two-parameter, or three-parameter model to ensure the accuracy of our predictions, without excessive parameters. In some cases, the higher order parameters were neglected if the lower order gave an adequate fit with acceptable sum of square residuals (SSR) while using non-linear regression analysis, and adding further parameters gave little improvement in the quality of the fit. It is important to note that the parameters of the Redlich-Kister model are purely empirical, having no physical meaning. Hence, whilst the quality of the fit, in a purely mathematical sense, is always improved by adding parameters, this is not necessarily justified on a physical basis. As parameters are added beyond a certain point, the fit starts to follow the random fluctuation in the data, and so the quality of the model can actually decrease by using too many parameters. How many parameters is required depends on the shape of the VLE curve and so judgement is required in selecting the appropriate number of parameters for the Redlich-Kister model. The two significant factors to consider are whether an extra parameter gives a significant improvement in the quality of fit (defined by a large reduction in SSR) and whether adding a parameter results in low frequency oscillations in the *P-x* curve, which is expected to be smooth over the whole range of compositions for physical systems. Hence the minimum number of parameters is used for each Redlich-Kister model to achieve a good fit, whilst avoiding oscillations in the *P-x* curve.

Table 4
Properties of pure components at 25 °C.

Pure components	MM (g/mol) (reference)	ρ (g/cm³) (reference)	η (cP) (reference)
Benzene	78.11 (Lide, 2005)	0.87 (Negadi et al., 2020; Petrino et al., 1995)	0.60 (Papaioannou et al., 1991)
Ethanol	46.07 (Dizechi & Marschall, 1982)	0.79 (Grgurić et al., 2004; Hwang & Robinson Jr, 1977)	1.08 (Canosa et al., 1998) (Chen & Tu, 2005)
Acetone	58.08 (Dizechi & Marschall, 1982)	0.79 (Puri et al., 1974) (Chen & Tu, 2005)	0.31 (González et al., 2005)
Methanol	32.04 (Dizechi & Marschall, 1982)	0.79 (Wanchoo & Narayan, 1992)	0.55 (Canosa et al., 1998)
Cyclohexane	84.16 (Lide, 2005)	0.77 (González et al., 2005) (Negadi et al., 2020)	0.89 (González et al., 2005; Papaioannou et al., 1991)
Acetonitrile	41.05 (Lide, 2005)	0.78 (Cunningham et al., 1967)	0.34 (Cunningham et al., 1967)
n-Hexane	86.18 (Lide, 2005)	0.66 (Iloukhani et al., 2005)	0.30 (Iloukhani et al., 2005)
Water	18.02 (Dizechi & Marschall, 1982)	1.00 (Cunningham et al., 1967)	0.89 (Lide, 2005)
Toluene	92.14 (Lide, 2005)	0.86 (Iloukhani et al., 2005)	0.55 (Iloukhani et al., 2005)

2.3. Self-diffusion coefficient, mutual diffusion coefficient, diffusion coefficient at infinite dilutions and viscosity data

Self-diffusion coefficient and experimental mutual diffusion coefficient data for the binary liquid phase mixtures are available from previous studies and literature and are summarized in Table 3. The graphs showing both viscosity and diffusion data are shown in the Supplementary Information while the properties of pure components are shown in Table 4.

For mixtures, when the composition (e.g., mole fraction) of a component in a mixture is infinitely close to zero, the diffusion

Table 5

Diffusivities at infinite dilute solution of different systems.

Component 1	Component 2	$D_{12}^{\infty}(10^{-9}m^2s^{-1})$	$D_{21}^{\infty}(10^{-9}m^2s^{-1})$
Benzene	Cyclohexane	1.92	2.08
Ethanol	Water	1.42	0.92
Acetone	Cyclohexane	2.34	3.85
Methanol	Ethanol	4.10	3.44
Cyclohexane	Ethanol	1.57	1.42
Acetonitrile	Water	1.69	5.52
Benzene	Acetone	3.96	2.68
Cyclohexane	Toluene	2.28	1.40
Ethanol	Benzene	2.01	1.46
Methanol	Benzene	2.89	2.41
n-Hexane	Toluene	2.58	4.24

coefficient of that component in this limit state is the diffusion coefficient of infinitely dilute concentration. The infinitely dilute concentrations of the diffusing components are generally obtained by extrapolation of the self-diffusion coefficient from literature. The values are represented in Table 5.

3. Results and discussion

3.1. Thermodynamics

The VLE data used for the thermodynamic modelling are reported in the Supplementary Information (Table S1a-d). The two different models employed separately help to establish the certainty of the thermodynamic correction factor with respect to determination of G^{ex} for the binary mixtures. The pressure-liquid composition fits of the studied systems are illustrated in the Supplementary Information (Fig. S1a-j). To obtain reliable results of the pressure-liquid data modelling, the Redlich-Kister model parameters were varied to give better fit with a minimum sum of squares residual values. For benzene-cyclohexane mixtures (Fig. S1a), the two-parameter model gave a better fit with minimum SSR with A and B values obtained as 0.48 and 0.03, respectively, while the NRTL model parameters G_{12} and G_{12} were obtained as 0.87 and 0.98, respectively. In ethanol–water mixture (Fig. S1b), the two-parameter R-K also gave a satisfactory result, with little improvement to the fit when both the third and fourth parameters are added to the modelling. Consequently, our R-K model parameters for ethanol–water were reported to be 1.1976 and −0.2818 for constants A and B, respectively, while the NRTL parameters were reported as 1.00 and 0.63 for G_{12} and G_{12}, respectively. This result agrees with those obtained by d'Avila and Silva (d'Avila & Silva, 1970) where they reported Redlich-Kister parameter values of 1.1976, −0.287, and −0.118 for constants A, B, and C, respectively. Similar results are obtained for the other mixtures (Fig. S1c-j) and the parameters for both models are reported in Table 6.

In the case of *n*-hexane-toluene, the VLE data could not be obtained; rather the Redlich-Kister parameter (Funk & Prausnitz, 1970) were directly used for the thermodynamic modelling to obtain the activity

coefficients and subsequently, the thermodynamic factor. As a result of the unavailability of the VLE data, the NRTL interaction parameters and local mole fractions could not be obtained for this mixture.

It is interesting to note that for most of the mixtures, both thermodynamic models gave similar quality of fit to the experimentally-obtained values.

Subsequently, the thermodynamic factor $1 + \frac{d\ln\gamma_1}{d\ln x_1}$ for both NRTL and Redlich-Kister models were plotted against the mole fractions of the diffusing components as illustrated in Fig. S2a-d. The results show similar plots for both models except in the case of methanol-benzene and cyclohexane-ethanol where there is a slight difference in the values obtained. This may be due to the relatively poor VLE fit at lower mole fractions of methanol and cyclohexane, respectively. One can conclude that the fit of the pressure-liquid data is quite sensitive to the underlying model, which is therefore an important factor to consider in the predictive diffusion model equations for these systems.

On the other hand, the similarity of correction factor plots for both NRTL and Redlich-Kister model of the same mixture is a strong indication that the thermodynamic factors are independent of the type of thermodynamic model used as long as a good VLE data fit is obtained for the modelling. The thermodynamic results obtained are further inputted into the diffusion model equations in order to predict the mutual diffusivities of the different systems.

3.2. Mutual diffusion predictions

All experimental mobility graphs consisting of diffusion and viscosity values obtained from literature are supplied in the Supplementary Information (Figure S3a-k).

In order to make a comprehensive evaluation of the prediction of the mutual diffusivities using the proposed seven diffusion models, the absolute average relative deviation of the predicted values from the experimental values is used as a criterion for the comparison. The individual final model predictions are compared with the reported values and the mean relative deviations calculated.

The absolute average relative deviation (AARD) of the model for a given system is the average of the relative deviations of the model-predicted diffusion coefficients from the experimental diffusion coefficients obtained from literature, at all concentrations, as defined by Eq. (41).

$$\text{AARD}(\%) = \frac{100}{N_p} \sum_{n=1}^{N_p} \frac{\left| D_{\text{exp}} - D_{\text{predict}} \right|}{D_{exp}} \tag{41}$$

where N_p is the number of experimental points.

As an example, in the case of *LM-SF* while predicting the benzene-acetone system with nine experimental points, the relative and mean deviations are shown in Table 7.

Then the average relative deviation of *LM-SF* for the benzene-acetone system can be calculated by Eq. (41) to give AARD = 0.9 %.

Table 6

Thermodynamic model parameters of the binary mixtures studied in this work.

Component 1	Component 2	NRTL		Redlich-Kister			
		G_{12}	G_{21}	A	B	C	D
Benzene	Cyclohexane	0.87	0.98	0.48	0.03	0.00	–
Ethanol	Water	1.00	0.63	1.20	−0.28	–	–
Acetone	Cyclohexane	0.55	0.55	1.80	0	0.16	0.04
Methanol	Ethanol	0.95	1.06	−0.05	–	–	–
Cyclohexane	Ethanol	1.63	0.67	−0.56	–	–	–
Acetonitrile	Water	0.64	0.75	1.98	0.14	0.07	–
Benzene	Acetone	0.80	0.98	0.45	0.05	0.04	0.01
Cyclohexane	Toluene	1.12	2.00	−2.28	−0.62	–	–
Ethanol	Benzene	0.68	0.40	1.78	−0.36	0.24	−0.10
Methanol	Benzene	0.57	0.34	1.97	–	–	–
n-Hexane	Toluene	–	–	0.54	−0.03	0.00	–

Table 7
Relative deviations of predicted diffusion coefficients (based on *LM-SF*) for NRTL-derived benzene-acetone systems.

x_1	$D_{exp}(10^{-9}m^2s^{-1})$	$D_{(LM-SF)}(10^{-9}m^2s^{-1})$	Relative deviation (%)
0.1	3.78	3.84	1.6
0.2	3.54	3.55	0.4
0.3	3.29	3.28	0.3
0.4	3.06	3.05	0.4
0.5	2.83	2.86	1.3
0.6	2.71	2.72	0.2
0.7	2.58	2.62	1.5
0.8	2.64	2.59	2.0
0.9	2.59	2.62	0.9

Analogously, the AARD of the seven chosen models for all binary systems are calculated, which helps to assess the performance of the models under a large range of forecasts. The results are highlighted in Tables 8 and 9 for NRTL and Redlich-Kister, respectively.

In predicting the mutual diffusivities of the local composition models (*LV* and *LM-SF*) using Redlich-Kister, the NRTL local mole fractions were used alongside the Redlich-Kister thermodynamic correction factor. This is to enable sufficient comparison and accuracy of our predictions.

It is evident from Tables 8 and 9 that for the prediction of these binary systems, the D-SF model, and the local compositions models *LM-SF* and *LV* have better performance with AARD values of 8.6 %, 9.3 %, and 13 %, respectively for the NRTL-derived models. For the Redlich-Kister, their values are 8.5 %, 9.6 %, and 10 %, respectively. Furthermore, the model based on infinitely dilute values of diffusion coefficients *Vis-SF* also performed relatively well with both having AARD values of 14 %. However, the effect of the removal of the scaling factor in the thermodynamic term in *Vis-nSF* is evident as the model gives considerably less accurate predictions of the mutual diffusivities for some of the mixtures compared to its parent model *Vis-SF*. The *V-Gex* model performed relatively poorly for most mixtures compared to the Darken-based models

except in the case of ethanol–water mixtures. Finally, *Dim-SF* performed poorly with very high AARD values for most mixtures except in cases with hydrogen-bonded network where one of the associating species is assumed to dimerize in the diffusing systems. The poor performance of the dimerization model is not surprising due to the fact that most mixtures would likely not form dimers during diffusion.

The subsequent sections give a detailed analysis of the various binary systems investigated in this work.

Benzene-cyclohexane

The diffusion coefficients predicted by the *Dim-SF*, based on formation of dimers, deviate significantly from the experimental values when predicting the diffusion coefficients for the benzene-cyclohexane system, as the mixture components do not exhibit strong association, implying a poor dimerization effect. This is illustrated in Fig. 1. For the NRTL-derived predictions, *D-SF*, *LV* and *LM-SF* models performed well with 0.6 %, 5.6 % and 6.5 %, respectively, compared to the infinitely diluted diffusion coefficients. *Vis-SF* also performed well, with a average relative deviation of 11 %. The good prediction performance of the self-diffusion based models *D-SF*, *LV* and *LM-SF* models with a scaling factor shows that they have identical suitability for this non-ideal system and are quite sensitive to mutual predictions. The suitability of these Darken-based models is a strong indication that the diffusing species behave like clusters. On the other hand, the high disparity in AARD of *Vis-SF* (11 %) and *Vis-nSF* (32 %) in the case of NRTL and *Vis-SF* (11 %) and *Vis-nSF* (26 %) for R-K is a strong indication that the scaling factor also plays an important role in predicting mutual diffusivity.

Ethanol-water

For this system, all models except *Vis-nSF* gave good predictions of the mutual diffusivities with the *D-SF, LM-SF,* and *LV* in increasing order as illustrated in Fig. 2. Interestingly, *Dim-SF* also performed well with an AARD value of 5.3 %, thus showing that for mixtures containing water this model performs relatively well, in agreement with previous preliminary findings (D'Agostino et al., 2012). This suggests that systems
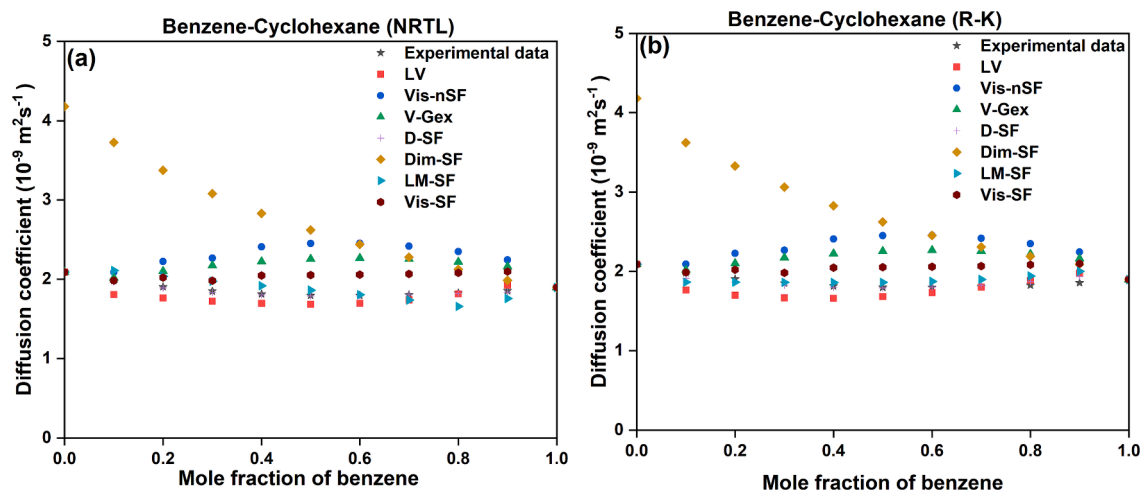
Table 8
NRTL-Derived AARD values of seven diffusion models.

Comp. 1	Comp. 2	LV	D-SF	Dim-SF	LM-SF	Vis-SF	V-Gex	Vis-nSF
		Absolute average relative deviation values (%)						
Benzene	Cyclohexane	5.6	0.6	47	6.5	11	18	32
Ethanol	Water	2.1	1.2	5.3	1.3	3.2	14	1.9
Acetone	Cyclohexane	20	19	16	9.5	16	58	35
Methanol	Ethanol	14	12	70	12	16	15	15
Cyclohexane	Ethanol	18	15	37	14	22	12	39
Acetonitrile	Water	5.5	5.9	8.3	6.5	5.3	45	20
Benzene	Acetone	5.6	3.6	47	0.9	1.5	9.6	60
Cyclohexane	Toluene	30	2.3	46	33	47	30	8.8
Ethanol	Benzene	23	23	27	7.9	18	43	24
Methanol	Benzene	4.3	3.3	2.7	1.8	1.4	7.4	68
Average (%)		**13**	**8.6**	**30.6**	**9.3**	**14**	**25**	**30**

Table 9
Redlich-Kister Derived AARD values of seven diffusion models.

Comp. 1	Comp. 2	LV	D-SF	Dim-SF	LM-SF	Vis-SF	V-Gex	Vis-nSF
		Absolute average relative deviation values (%)						
Benzene	Cyclohexane	4.7	1.8	47	2.3	11	18	26
Ethanol	Water	2.2	1.3	5.2	1.3	3.3	14	1.9
Acetone	Cyclohexane	11	20	15	9.9	16	57	35
Methanol	Ethanol	15	12	70	12	16	15	15
Cyclohexane	Ethanol	16	15	22	14	22	12	42
Acetonitrile	Water	5.6	4.1	8.4	5.2	3.6	45	20
Benzene	Acetone	5.7	4.4	49	1.4	1.5	9.4	61
Cyclohexane	Toluene	21	2.4	47	21	48	31	8.7
Ethanol	Benzene	18	27	28	23	19	43	24
Methanol	Benzene	7.0	3.9	5.4	6.7	6.2	7.4	65
n-Hexane	Toluene	–	2.3	53	–	13	28	31
Average (%)		**10**	**8.5**	**32**	**9.6**	**14**	**25**	**30**

Fig. 1. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for benzene-cyclohexane mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
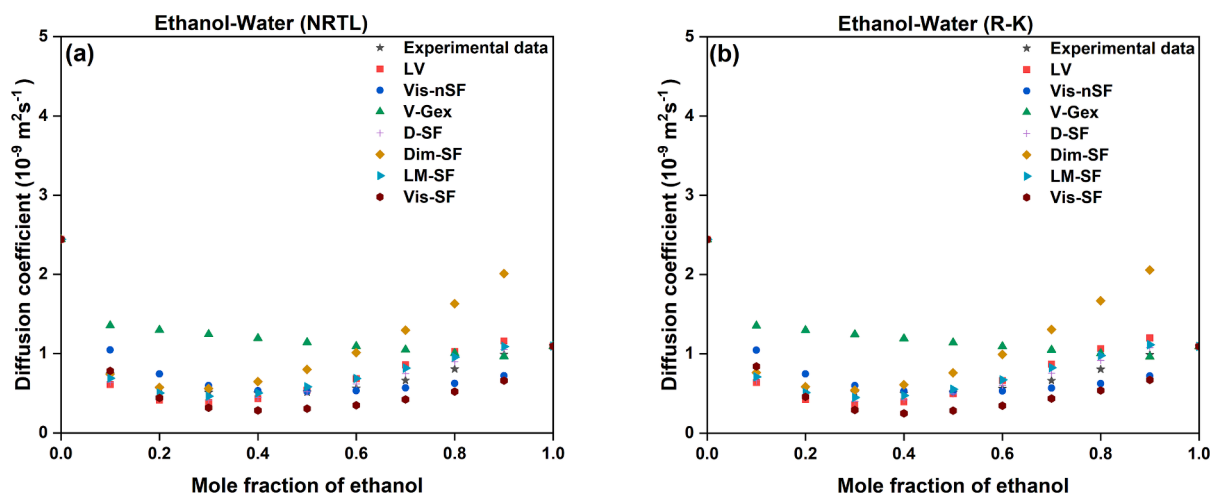

Fig. 2. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for ethanol–water mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
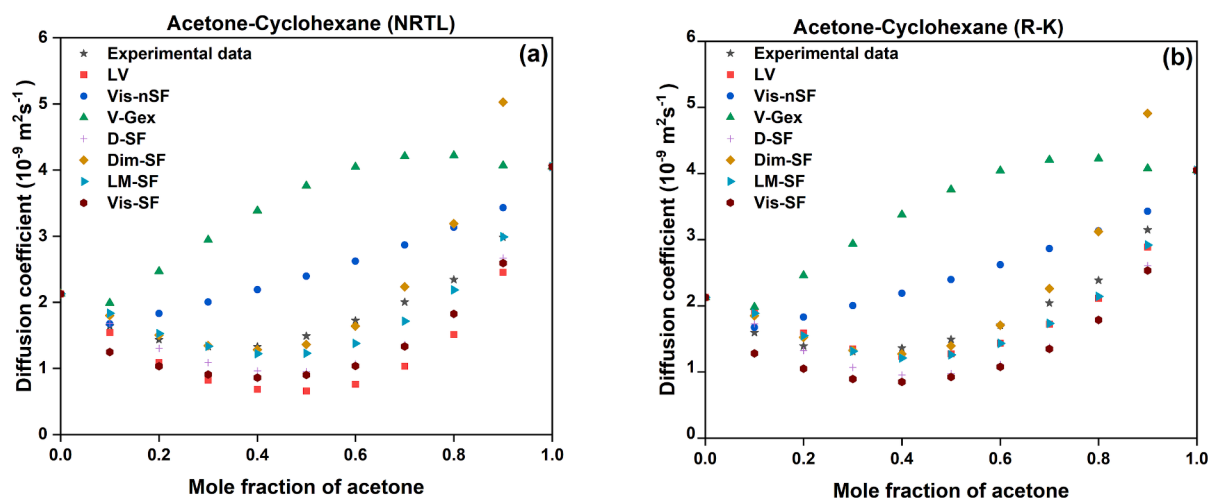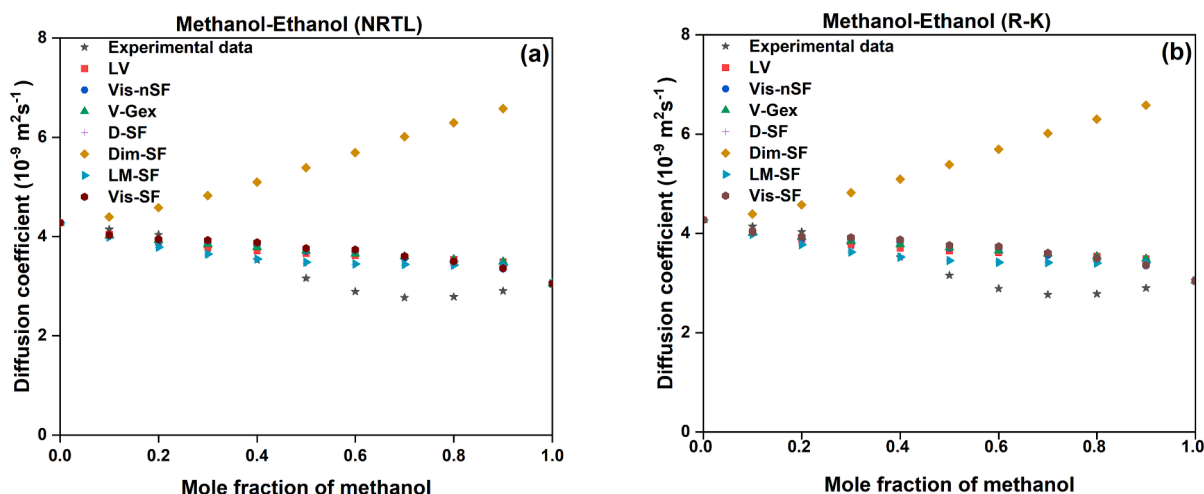

Fig. 3. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for acetone-cyclohexane mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.

Fig. 4. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for methanol-ethanol mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.

able to form hydrogen bonding interactions may lead to the formation of dimers (Moggridge, 2012a), hence the better accuracy of this model. The relative similarly in prediction values indicates that the movement between ethanol and water molecules are highly correlated over the entire composition range and are independent of the nature of the transport property used in the prediction. Zhang and Yang (Zhang & Yang, 2005) reported that there are basically four interaction sites of the ethanol molecule consisting of the oxygen and hydrogen atoms, and the methyl and methylene groups, while the behaviour of water molecules in the mixture is ascribed to both "bound" and "free" water contributions leading to formation of loosely-held complexes (Dunstan, 1904) *via* dipole–dipole interactions or hydrogen bonds (Nikumbh & Kulkarni, 2013). However, the Vignes-Based model *V-Gex* has a higher AARD (14 %) compared to other models indicating that the thermodynamic potentials of this system in the form of the Gibbs free energy is the source of the inaccuracy and has been circumvented with the introduction of the thermodynamic correction factor. Thus, the thermodynamic effect (Coelho et al., 2002) is an important variable to consider.

Acetone-cyclohexane

For the acetone-cyclohexane system shown in Fig. 3, the best prediction performance was achieved by *LM-SF* with an AARD of 9.5 %, followed by *Vis-SF* with AARD of 16 %. Different experimental values

(Bosse & Bart, 2006; Tasić et al., 1978) were compared with the predicted models that gave similar AARD values, with *V-Gex* being the least satisfactory. Good prediction for the *Dim-SF* at lower acetone mole fractions ($0 < x_1 \leq 0.61$) was also observed, suggesting strong association of acetone molecules at low mole fractions. Puri at al. (Puri et al., 1974) also reported the formation of an azeotrope at ($x_1 = 0.74$), indicating strong attractive forces within the fluids up to this concentration. This also explains the best predictive performance of *LM-SF* as it is based on the assumption of formation of strong intermolecular interactions resulting in a highly-correlated movement of diffusing molecules. In addition, the infinitely-dilluted-based model with a scaling factor (*Vis-SF*) gave identical fitting to the self-diffusion-based models indicating the consistency in the transport properties. However, the impact of the thermodynamic correction factor was observed in the viscosity-based models (*Vis-SF* and *Vis-nSF*) with *Vis-nSF* having AARD more than twice in value of *Vis-SF*. The Vignes-based model *V-Gex* gave poor prediction for this system, which further highlights the influence of thermodynamics on the diffusional behaviour in non-ideal systems.

Methanol-ethanol

All models except *Dim-SF* performed well with AARD values between 11 and 15 % (Fig. 4). However, at higher mole fractions, there is a slight deviation of all models from the experimental mutual diffusion values.
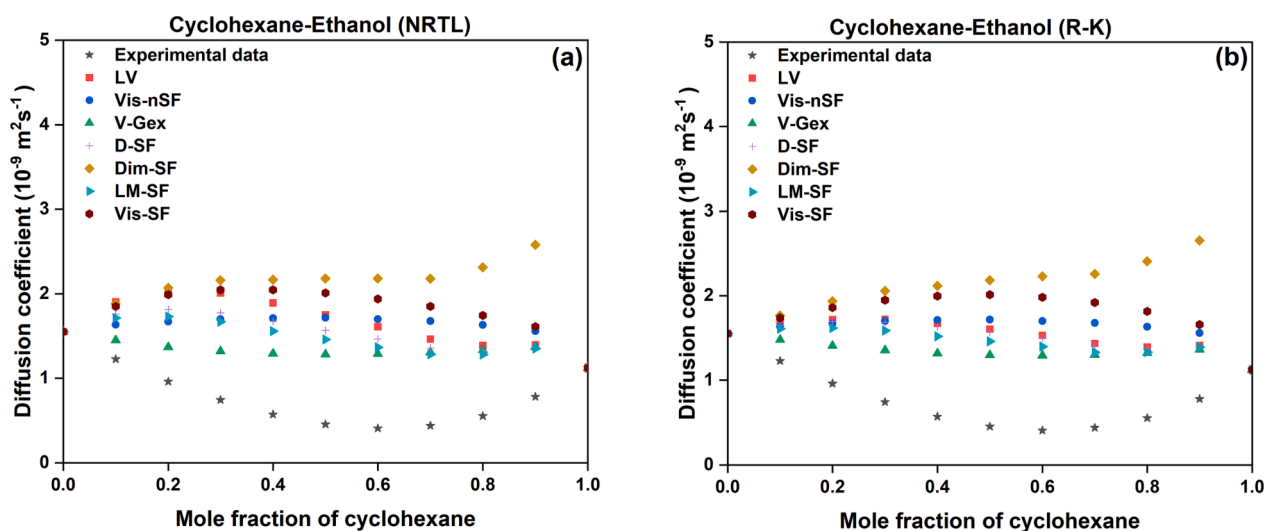

Fig. 5. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for cyclohexane-ethanol mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
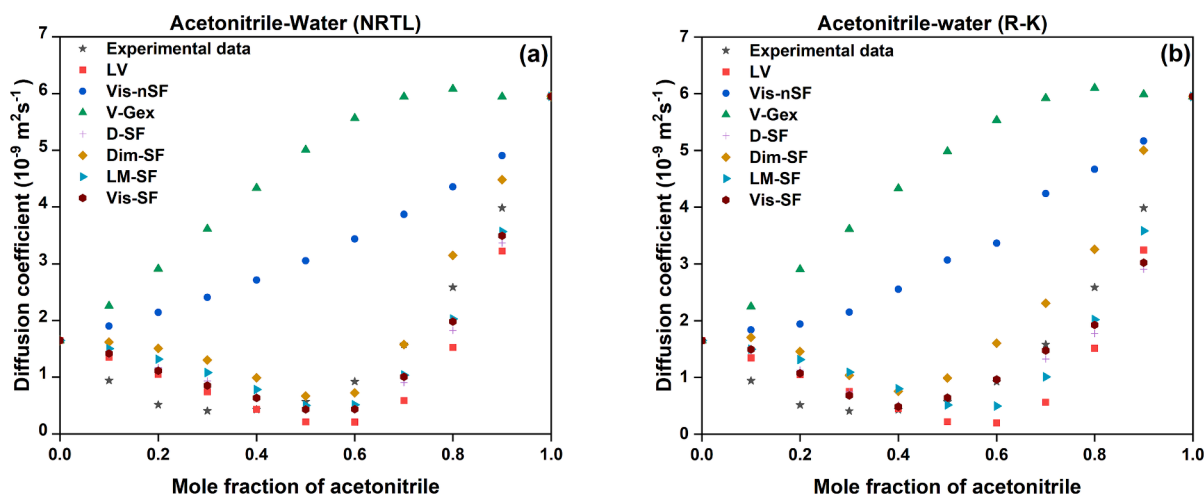
Fig. 6. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for acetonitrile–water mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.

Lone et al. (Lone et al., 2008) investigated the dielectric parameters of methanol-ethanol mixtures in order to study the effect and nature of molecular interactions existing between both polar molecules. In their study, they reported that the static dielectric constant ε_o decreases while the relaxation time τ increases with an increase in the mole fraction of ethanol. The non-linear variations in the excess properties, such as excess dielectric constants ε_E and relaxation times, is an indication that there is a strong intermolecular association taking place within the system via hydrogen bonding and dipole–dipole interactions. However, our prediction models indicate there is no dimerization effect in the mixture but rather strong intermolecular interactions behaving like an ideal system due to similar molecular structures.

Cyclohexane-ethanol

For the cyclohexane-ethanol system as shown in Fig. 5, all models failed to predict the mutual diffusion coefficient accurately. It is however, observed that all predicted models behaved similarly except the experimental mutual diffusion values. Hence, the discrepancies between predicted and experimental data reported for this mixture could be due to errors and less accurate experimental data obtained from literature.

Acetonitrile-water

For the acetonitrile–water system, the local composition models performed well and gave a good prediction of the mutual diffusivities as shown in Fig. 6. However, *V-Gex* and *Vis-nSF* models performed poorly.

As expected, the dimerization model *Dim-SF* performed well due to the aprotic nature of acetonitrile molecule, which dissolves in water at all concentrations (Takamuku et al., 1998). In acetonitrile–water mixtures, both water and acetonitrile clusters coexists (Kovacs & Laaksonen, 1991), resulting in microheterogeneity in the mixtures. Microheterogeneity occurs when molecules of a particular component is preferentially surrounded by molecules of the same kind (Von Goldammer & Hertz, 1970); in this case, dimerization likely occurs. It is worth noting that in acetonitrile–water interactions, there exists dipole–dipole interactions and weak hydrogen bonding between acetonitrile and water molecules in the range $0.2 < x_1 < 0.8$ (Saleh et al., 2006) as well as the presence of multiple acetonitrile-hydrate clusters in mixed solutions.

Benzene-acetone

For this mixture, the local composition models peformed very well with AARD values between 1 and 6 % when both NRTL and Redlich-Kister are used for thermodynamic modelling. The viscosity and infinitely-diluted models show similar AARD values. However, both *Dim-SF* and *Vis-nSF* models failed to give good predictions with very high AARD values between 47 and 61 %, as illustrated in Fig. 7. In addition, the wide disparity in AARD values between *Vis-SF* (1.5 %) and *Vis-nSF* (60 %) shows the importance of the scaling factor in the thermodynamic term of the mutual diffusivity equations. The nature of the mutual
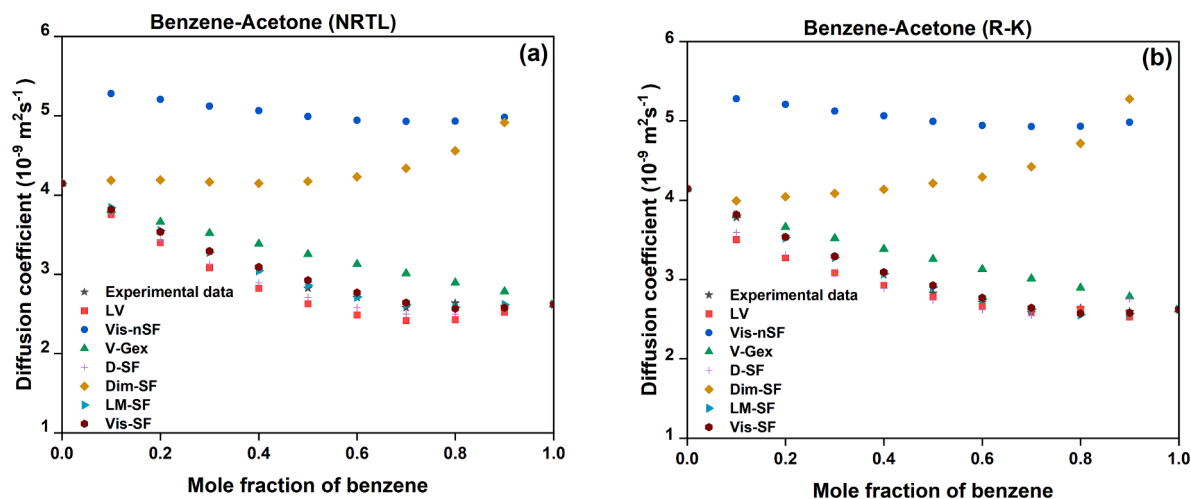

Fig. 7. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for benzene-acetone mixtures using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
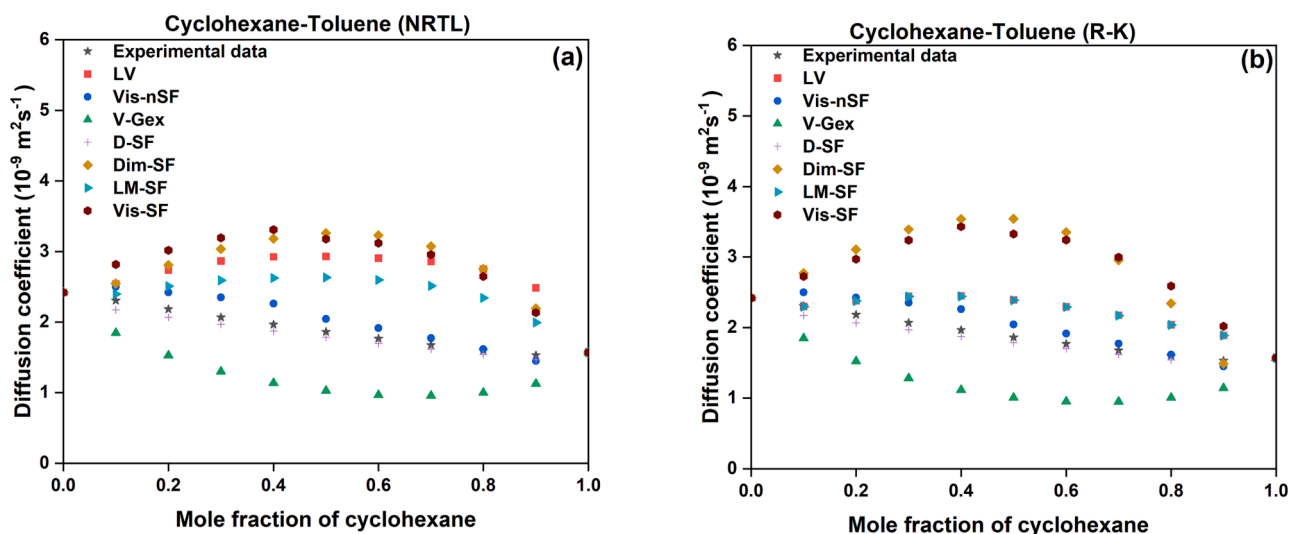
Fig. 8. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for cyclohexane-toluene mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
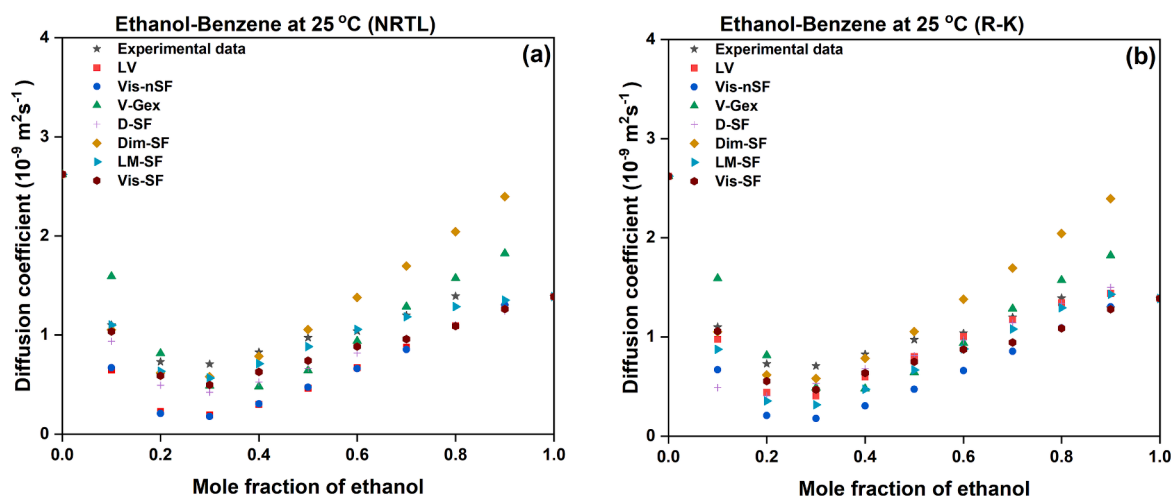

Fig. 9. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for ethanol–benzene mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.

diffusion coefficients graphs show a moderate decrease with a slight curvature centered close to the equimolar composition indicating solvation effects due to the methyl and oxygen sites of acetone molecules (Guevara-Carrion et al., 2016).

Cyclohexane-toluene

The behaviour of the different diffusion models are illustrated in Fig. 8. For the cyclohexane-toluene system, *D-SF* accurately predicts the mutual diffusion coefficients with 2.3 % and 2.4 % AARD for NRTL- and Redlich-Kister derived modelling, respectively; closely followed by *Vis-nSF* with a value of 8.7 %. In the case of Redlich-Kister, the local volume *LV* and local mole *LM-SF* models gave similar (21 %) but higher AARD values compared to *D-SF* indicating that there are significant volume changes due to mixing. The dimerization model also performed poorly indicating no dimerization effect in the mixture. The ability of the self-diffusion-based model *D-SF* to accurately predict the mutual diffusivity of this aliphatic–aromatic system indicates that in addition to the choice of the G^{ex} model used, the individual properties of the liquids also play a dominant role compared to the collective properties such as viscosity.

Ethanol-benzene

For this system, all prediction models show a similar pattern, as illustrated in Fig. 9 with AARD values in the range of 17–28 %. This may

be due to the uncertainty in the experimental data used in comparison. The dimerization model does reasonably well at low mole fractions of ethanol up to 0.5. However, as the composition of ethanol increaes, there is a strong deviation from experimental values.

Methanol-benzene

The results for this mixture are shown in Fig. 10. All models gave an acccurate prediction (4–7 %) of the mutual diffusion coefficients, which can be explained by the presence of favorable interaction energy between the –OH group of methanol and the π-electrons of the aromatic benzene molecule leading to increasing breakage of the hydrogen bonds of methanol (Smith & Robinson Jr, 1970). However, the *Vis-nSF* model was inaccurate and gave a poor prediction. This can be attributed to the absence of the scaling factor in its thermodynamic correction term.

n-Hexane-toluene

Due to the unavailability of the VLE data for this mixture, the Redlich-Kister thermodynamic parameters were instead obtained from literature and were subsequently used for calculating the activity coefficients. Hence, only the Redlich-Kister derived models were used for predictions as it was not possible to obtain the NRTL parameters. From Fig. 11, it is seen that *D-SF* model gave an excellent prediction of the mutual diffusivities with an AARD value of 2.3 %. The dimerization
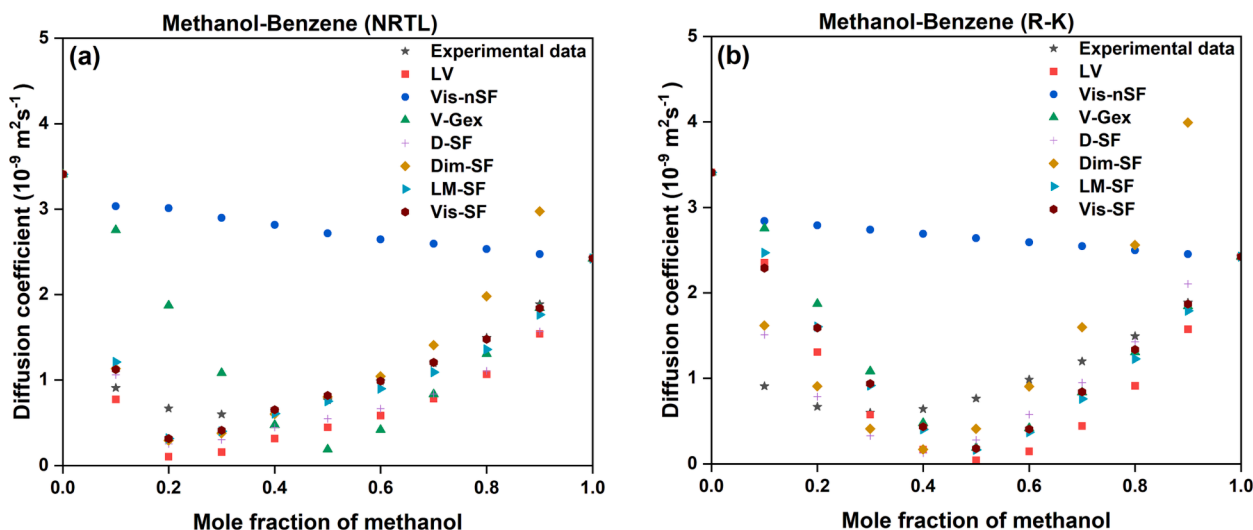
Fig. 10. Comparison of experimental and predicted mutual diffusion coefficients with different diffusion models for methanol-benzene mixtures at 298.15 K using (a) NRTL and (b) Redlich-Kister thermodynamic modelling.
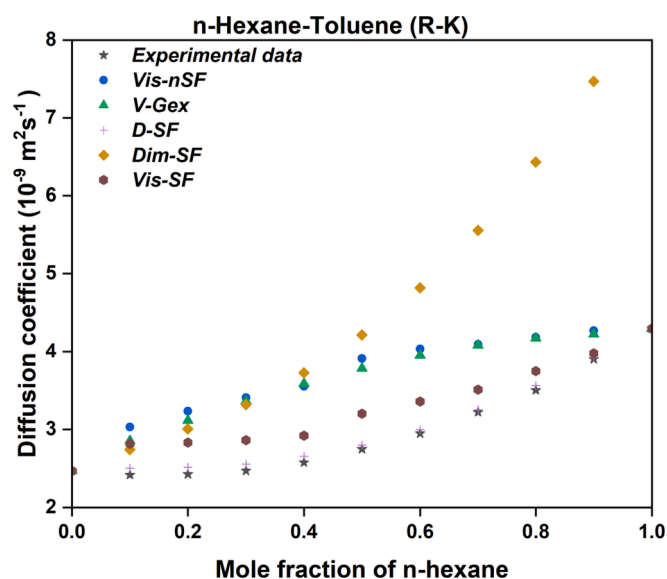

Fig. 11. Comparison of predicted mutual diffusion coefficients with different models for *n*-hexane-toluene mixture at 298.15 K using the Redlich-Kister thermodynamic model.

model *Dim-SF* gave the least accurate performance with a value of 53 %, while the viscosity-based model with no scaling factor *Vis-nSF* has a value of 31 %.

The accuracy of each model in predicting the diffusion coefficients of binary mixtures was assessed and the graphical representation is illustrated in Fig. 12.

Different prediction models have their own strengths and weaknesses for different systems. However, for the whole range of mixtures studied, *D-SF* was the most accurate among the models analyzed, followed closely by the local composition models: *LM-SF* and *LV*. The AARD values for *D-SF*, *LM-SF*, and *LV* for NRTL model are: 8.6 %, 9.3 %, and 13 %, respectively; while those of R-K model are: 8.5 %, 9.6 %, and 10 %, respectively. This suggests that the use of measurements involving self-diffusion coefficients (an individual microscopic property) as a function of composition and local mole fractions works well in predicting mutual diffusivities of mixtures when compared to the use of measurements of viscosity (collective macroscopic property).

In addition, the quality of the VLE data and the choice of the G^{ex} model employed in a model plays a significant role in mutual diffusion predictions. Most importantly, the thermodynamic correction factor is the dominant and sensitive parameter to be considered in these modelling.

Thus, based on the prediction results obtained, Table 10 gives a summary and guidance of the type of model approach to be used for different types of systems.

4. Conclusion

This paper investigates the predictive power of several models used for predicting mutual diffusivities, while testing the models using the thermodynamic scaling power, and the thermodynamic factors obtained from two different thermodynamics models, NRTL and Redlich-Kister. The models are tested for eleven binary mixtures. Seven approaches are used, which are the local composition models: *LV* and *LM-SF*; the dimerization model *Dim-SF*, the darken-based model *D-SF*, the inifinitely-diluted and viscosity-based models: *Vis-SF* and *Vis-nSF*; and the Vignes-based model *V-Gex*.

The dimerization model *Dim-SF* has shown a relatively large error except in mixtures with strongly associative components such as ethanol–water and acetone-cyclohexane mixtures. The relatively poor performance of *Vis-nSF* when compared to *Vis-SF* is largely due to the absence of a scaling factor in the former's thermodynamic term. This, therefore, underscores the importance of considering a thermodynamic correction factor in the thermodynamic term when using prediction models for mutual diffusivity.

Finally, the choice of the thermodynamic model used for calculating the thermodynamic factor does not affect significantly prediction performances as long as a good fit is obtained when constructing the activity coefficient model from the VLE data.

CRediT authorship contribution statement

Olajumoke Alabi-Babalola: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jie Zhong:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Geoff D. Moggridge:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Formal analysis. **Carmine D'Agostino:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation,
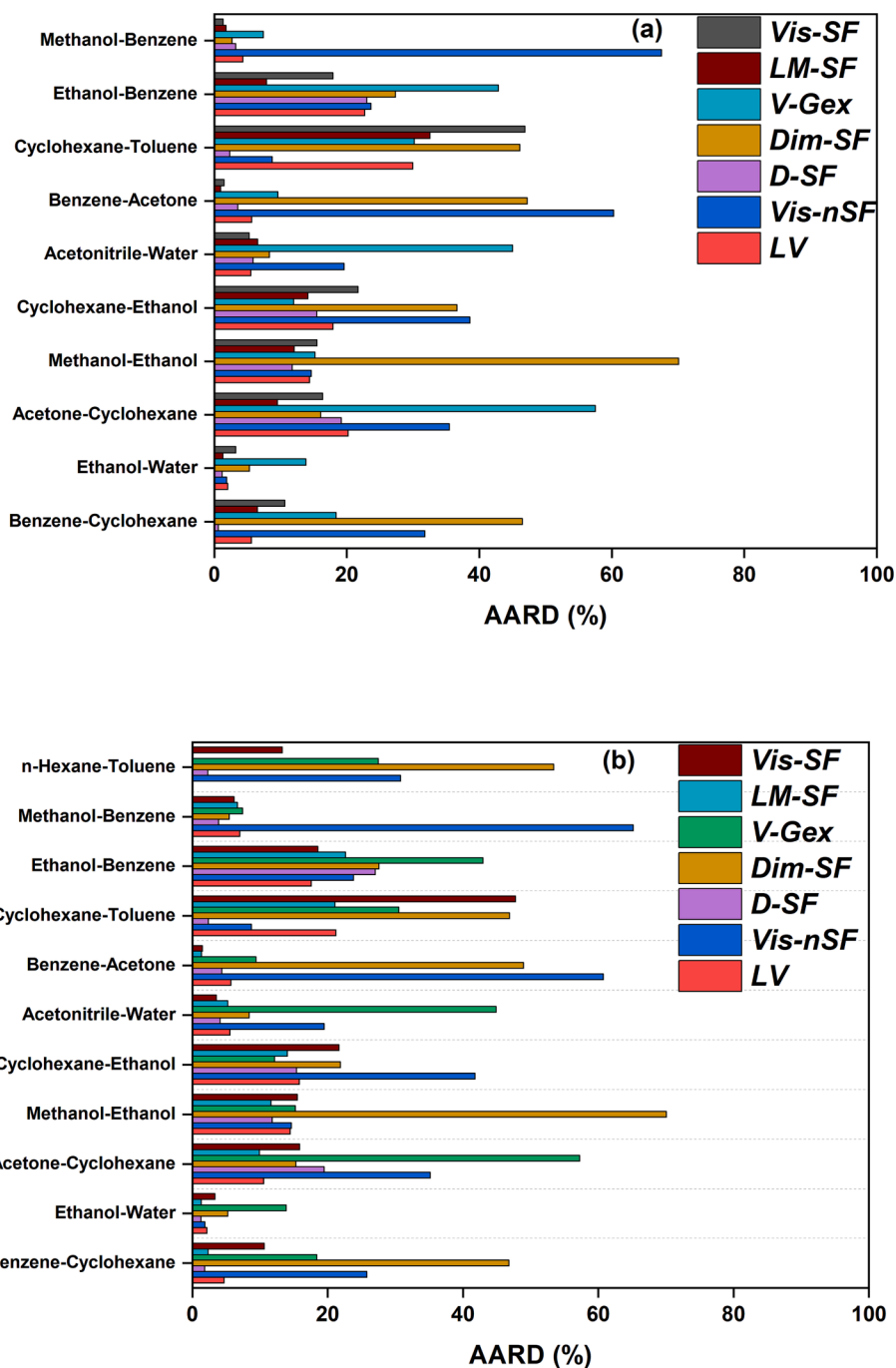
Fig. 12. Performance indicator of seven different diffusion models (a) NRTL (b) Redlich-Kister.

Table 10
Model recommendation for different types of systems.

Type of system	Recommended model(s)
Aromatic-cyclic hydrocarbons	*D-SF*
Water-containing mixtures	All models with a thermodynamic scaling factor
Ketone-cyclic hydrocarbons	Local composition models: *LM-SF, LV*
Polar hydroxy components	All models
Alcohol-cyclic hydrocarbons	*D-SF*
Aromatic-ketones	*LM-SF, LV, D-SF, Vis-SF*
Aromatic-alcohols	All models with a thermodynamic scaling factor
Aromatic-long chain hydrocarbons	*D-SF*

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2024.119930.

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