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DEVELOPMENT OF A MORE PREDICTIVE CUBIC PLUS ASSOCIATION EQUATION OF STATE

PEDRO VELHO FERREIRA
DISSERTAÇÃO DE MESTRADO APRESENTADA
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO EM
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Master of Science in Chemical Engineering

Development of a more predictive Cubic Plus Association equation of state

A Master's Dissertation of

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Developed within the course of Dissertation (EQ0107) and held at:

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Preface

As a requisite to obtain the Master's degree in Chemical Engineering at the Faculty of Engineering of the University of Porto, this document, carrying the load of 30 ECTS, was prepared. It reports the results of a project developed at the Center for Energy Resources Engineering (CERE) at the Technical University of Denmark, Denmark, in close collaboration with the Associate Laboratory Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM) of the University of Porto, Portugal, and under the Erasmus+ Programme.

Furthermore, having in mind that the presentation in Portugal will represent the majority of the grade, this document follows the University of Porto's template. Although, it was written so as to respect both Danish and Portuguese rules to the highest extent possible.

Throughout this document, some units are not presented in the International System of Units (SI). The reason for this is to keep consistency with units used in previous works related to the Cubic Plus Association equation of state.

Lastly, it is hereby declared under word of honour that it is original and that all the non-original contributions were properly referenced with source identification.

Pedro Velho Ferreira

6 July 2020

Acknowledgements

During our lives, there are hands which take and hands which give, even though, some times, quite surprisingly, by taking they are actually giving and by giving they are innocently taking.

To the ones who tirelessly gave and never willingly took, especially to my family and friends, in a somewhat general but also very specific remark, a public thank you and a colossal desire of fulfilling expectations. To the supervisors at DTU, Prof. Georgios Kontogeorgis and Assoc. Prof. Xiaodong Liang, and to CERE's personnel, thank you so much for accepting and integrating me, for continuously pushing my limits and for always being eager to explain concepts and broaden horizons. To the supervisors at FEUP, Prof. Maria Eugénia Macedo and Dr. Elena Gómez Costas, as well as LSRE-LCM's entire team, my endless gratitude for believing since the beginning, for all the last years' support and shared knowledge and for never being farther away than a phone call.

I also want to express deep gratitude for the scientific initiation fellowship the Associate Laboratory LSRE-LCM granted me from September to December 2019. The project, financed by UID/EQU/50020/2019 and named "Study of the recovery of flavonoids using novel ethyl lactate-based aqueous two-phase systems with biodegradable citrate salts", helped consolidating knowledge and creating good work habits, which became very useful during the development of this Master's thesis.

A man can only be whole when he is a part of something and I feel indivisible.

”La nuossa lhéngua

Armanos cantai an charro,
Na nuossa lhéngua q’hardemos;
La fala de nuossos pais
Yé l Pertués que tenemos.

Ah! Fala nuossa i siempre biba,
Falada i nunca screbida!...
Tu sós
La mais rica eiterna i nobre hardança
Q’an beisos de criança
Me dórun cul pan negro
Mius pais i mius abós.

Falai-la, mius armanos.
Guardai-la!...
Stimai-la!...
(...)”

António Maria Mourinho

(Written in Mirandese, the 2nd Official Language of Portugal)

Abstract

This project aimed to increase the predictability of the Cubic Plus Association (CPA) equation of state, a model which puts together the Soave-Redlich-Kwong (SRK) equation of state with the association term of the Wertheim theory. The CPA EoS requires some parameters to accurately describe the behaviour of chemical compounds. Specifically, three parameters are required for non-associating compounds, i.e., which don't establish hydrogen bounds, (co-volume, b, and the energy parameters a_0 and c_1) and five for associating compounds (a_0, b, c_1, the association energy, ε, and the volume of association, β). However, a high number of parameters is still unknown, especially in electrolytes, ionic liquids, pharmaceuticals, polymers and other heavy compounds, so there is a significant need of finding ways of predicting them.

After establishing a database with 197 chemical compounds, correlations for parameters and properties were searched for between groups of similar species. For example, very good second-degree correlations were found for all the compounds except fluorocarbons for a_0 with the van der Waals volume, V_w, ($R^2 = 0.9941$), for b with V_w ($R^2 = 0.9973$) and for b with a_0 ($R^2 = 0.9925$). The linear correlation of b with V_w was also very good ($R^2 = 0.9928$). In alkanes, probably because of their particular regularity, additional correlations were found. Whenever absent in the literature, the values for the van der Waals volumes and surface areas were determined following Bondi's method, and, in general, the former showed better correlations than the latter. Finally, a_0 also showed higher determination coefficients than Γ and with simpler mathematical functions.

Following, four different methods were used in predicting vapour pressure and liquid density. The first used only CPA EoS parameters from the literature, the second used correlated values of Γ and b, the third used the same correlated parameters and fitted c_1 and the last one correlated b and fitted both Γ and c_1. The predicted values were compared to data from the Design Institute for Physical Properties and a range from $0.5 \cdot T_c$ to $0.95 \cdot T_c$ with a step of 1 K was considered. In about 46 000 convergences, liquid densities with average absolute deviations (AAD) of 3.7 %, 54.9 %, 14.1 % and 1.5 % and vapour pressures with AAD of 2.0 %, 6.0 %, 4.7 % and 3.7 % were obtained using the four methods, by ascending order. Hence, in the prediction of the vapour pressure the results could be strongly affected by replacing a_0 and b by their correlated versions.

Then, the exponents n for 219 binary interaction parameters (k_{ij}) were calculated using the Hudson-McCoubrey theory and following two different methods, one being the "classical" theory and the other an approximate expression not considering the ionisation potentials. In general, values between 0 and 10 were obtained and were especially good for asymmetric compounds. This is interesting since this theory would be applied with predictive purposes in compounds with high asymmetry and unknown properties. Further, the second method ended up being a very good alternative whenever needed, correctly describing the species' behaviours even though it had a simplified mathematical expression. Later, the relationship between the calculated exponents and measures of asymmetry, as the ratio of co-volumes and of van der Waals volumes, were studied. Very good relations were found between the exponents n and the measures of asymmetry between alkanes and alcohols, glycols, polyols, acetic acid, ethanol and water and between acetone-hydrocarbons. Although not so common, some correlations were also found for k_{ij} with measures of asymmetry. In conclusion, by exploring the common behaviour of the properties of similar compounds, the predictability of the CPA EoS model was successfully enlarged while still presenting a good performance.

Keywords: CPA EoS; Predictive Model; Hudson-McCoubrey.

Resumo

Neste projeto, pretendeu-se aumentar a preditibilidade da equação de estado *Cubic Plus Association* (CPA), um modelo constituído pela equação de estado Soave-Redlich-Kwong (SRK) e pelo termo associativo de Wertheim. Esta equação de estado requer vários parâmetros para conseguir descrever corretamente o comportamento dos compostos químicos, nomeadamente, o co-volume, b, e os termos energéticos, a_0 e c_1, em componentes não-associativos, i.e., que não estabelecem pontes de hidrogénio. Adicionalmente, o volume de associação, β, e a energia de associação, ε, são necessários para compostos associativos. No entanto, muitos destes parâmetros são desconhecidos, especialmente em eletrólitos, líquidos iónicos, produtos farmacêuticos, polímeros e demais compostos de elevada massa molecular, pelo que é necessário prevê-los.

Primeiramente, foi criada uma base de dados com 197 espécies químicas, na qual se procurou estabelecer correlações. Por exemplo, relações de segundo grau foram obtidas para todos os compostos à exceção dos fluorocarbonos entre a_0 e o volume de van der Waals, V_w, (R^2 = 0.9941), entre b e V_w (R^2 = 0.9973) e entre b e a_0 (R^2 = 0.9925). Por outro lado, uma boa relação linear também foi encontrada entre b e V_w (R^2 = 0.9928). Em alcanos, devido à sua regularidade, várias outras correlações foram encontradas. Quando indisponíveis na literatura, a área superficial de van der Waals (A_w) e V_w foram estimados usando o método de Bondi, uma metodologia de contribuições de grupo. Em regra, V_w apresentou correlações com maior coeficiente de determinação do que A_w e o mesmo pode afirmar-se sobre a_0 em relação ao termo energético corrigido, Γ.

Seguidamente, quatro métodos foram aplicados na previsão de pressão de vapor e massa volúmica líquida. O primeiro usou apenas parâmetros CPA da literatura, o segundo usou dois parâmetros correlacionados (Γ e b), o terceiro fez uso dos mesmos correlacionados e ajustou c_1 e o quarto ajustou c_1 e Γ e usou b de correlações. Todos os valores foram comparados com dados da base do *Design Institute for Physical Properties* (DIPPR), sendo que um intervalo de $0.5 \cdot T_\mathrm{c}$ a $0.95 \cdot T_\mathrm{c}$ com um passo de 1 K foi considerado. Em cerca de 46 000 pontos, as massas volúmicas líquidas foram determinadas com erros absolutos médios de 3.7 %, 54.9 %, 14.1 % e 1.5 % e as pressões de vapor de 2.0 %, 6.0 %, 4.7 % e 3.7 % com os quatro métodos, por ordem crescente. Assim sendo, foi notório que o cálculo da pressão de saturação é muito sensível a correlacionar-se a_0 e b.

Então, os expoentes n de cada um dos 219 parâmetros de interação binária (k_{ij}) foram calculados aplicando a teoria de Hudson-McCoubrey e seguindo dois métodos distintos, sendo que o primeiro usou a sua forma "clássica" e o segundo uma expressão aproximada que não considerava os potenciais de ionização. Na maioria dos casos, valores entre 0 e 10 foram obtidos, com resultados especialmente bons em compostos assimétricos, o que constitui um resultado ótimo, uma vez que se pretende aplicar este método preditivo em compostos de propriedades desconhecidas e pares de componentes altamente assimétricos. O segundo método relevou-se uma alternativa muito boa ao primeiro, descrevendo corretamente os sistemas, apesar da sua expressão simplificada. Posteriormente, estudou-se a relação entre os expoentes calculados e algumas medidas de assimetria, como é o caso da razão de volumes de van der Waals e de co-volumes, sendo que boas correlações foram encontradas em combinações de alcanos com álcoois, glicóis, polióis, ácido acético, etanol e água e em acetona-hidrocarbonetos. Apesar de mais incomuns, também foram encontradas algumas relações entre k_{ij} e as medidas de assimetria. De forma sucinta, alargou-se a capacidade de previsão da equação CPA tirando proveito do comportamento comum das propriedades de compostos similares e mantendo o seu bom desempenho.

Palavras-chave: CPA; Modelo Preditivo; Hudson-McCoubrey.

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List of Abbreviations and Symbols

A	Type of hydrogen bonding site	-
A_w	van der Waals surface area	cm^{2}·mol^{-1}
a	Energy parameter	Pa·m^{6}·mol^{-2}
a_0	Energy term parameter	Pa·m^{6}·mol^{-2}
a_{ij}	Cross energy parameter between molecules i and j	Pa·m^{6}·mol^{-2}
B	Type of hydrogen bonding site	-
b	Co-volume parameter	L·mol^{-1}
b_{ij}	Cross co-volume between molecules i and j	L·mol^{-1}
b_ratio	Bigger co-volumes ratio	
c_1	Energy term parameter	
G^E	Excess Gibbs free energy	J
g^E	Molar excess Gibbs free energy	J·mol^{-1}
g	Radial distribution function	
I	Ionisation potential	eV
k_{ij}	Binary interaction parameter between molecules i and j	
k_1	Equation adjustable parameter	
k_2	Equation adjustable parameter	
k_3	Equation adjustable parameter	
k_4	Equation adjustable parameter	
L_1	Example of dependent variable	-
L_2	Example of independent variable	-
l_d	Bond distance	m
N_C	Number of compounds	
N_D	Number of data points	
N_i	Total number of groups i in a specific molecule	
P	Pressure	Pa
P_c	Critical pressure	Pa
Q_i	Relative van der Waals molecular surface area contribution of group i	
q	Relative van der Waals molecular surface area	
R^2	Determination coefficient	
R_i	Relative van der Waals molecular volume contribution of group i	
R_g	Ideal gas constant	J·mol^{-1}·K^{-1}
r	Relative van der Waals molecular volume	
r_w	Intermolecular van der Waals radius	m
T	Temperature	K
T_c	Critical temperature	K
T_r	Reduced temperature	
t	Total number of elements	

V_{m}	Molar volume	$\mathrm{m^3 \cdot mol^{-1}}$
V_{ratio}	Bigger van der Waals volumes ratio	
Y_{DIPPR}	Generic predicted given by DIPPR correlations	
Y_{method}	Generic predicted property	
V_{w}	van der Waals volume	$\mathrm{cm^3 \cdot mol^{-1}}$
X_{A}	Fraction of sites A which are not bounded to other active sites	
x	Molar fraction	
Z	Compressibility factor	
$Z^{\mathrm{association}}$	Compressibility factor of association	

Greek letters

$\beta^{A_iB_i}$, $\beta^{A_jB_j}$	Association volume	
β	Cross-association volume (simplified)	
$\beta^{A_iB_j}$	Cross-association volume	
Γ	Corrected energy parameter	K
$\Delta_{A_iB_j}$	Association strength between site A on i molecule and B on j molecule	$\mathrm{m^3 \cdot mol^{-1}}$
$\varepsilon^{A_iB_i}$, $\varepsilon^{A_jB_j}$	Association energy	$\mathrm{J \cdot mol^{-1}}$
ε	Cross-association energy (simplified)	$\mathrm{J \cdot mol^{-1}}$
$\varepsilon^{\mathrm{LJ}}$	Energy parameter	$\mathrm{J \cdot mol^{-1}}$
$\varepsilon^{A_iB_j}$	Cross-association energy	$\mathrm{J \cdot mol^{-1}}$
ε_{ij}	Unlike energy parameter	$\mathrm{J \cdot mol^{-1}}$
ζ	Group contribution calculation constant	
Ω	Group contribution calculation constant	
ω	Acentric factor	
ρ	Molar density	$\mathrm{mol \cdot m^{-3}}$
ρ_{L}	Liquid density	$\mathrm{kg \cdot m^{-3}}$
σ	Size parameter	Å
σ_{ij}	Unlike size parameter	Å
W	General property used as an example	-

Indexes

corr.	Correlated
cross.	Cross-association
exp.	Experimental
fit.	Fitted
i	Index or counter
j	Index or counter
k	Index or counter
sat.	Saturation

Abbreviations

AD	Absolute deviation
AAD	Average absolute deviation
AM	Arithmetic mean
APACT	Associated Perturbed Anisotropic Chain Theory
BTEX	Benzene, toluene, ethylbenzene and xylene
CERE	Center for Energy Resources Engineering
CPA	Cubic Plus Association
CR-1	Combining rule 1
DIPPR	Design Institute for Physical Properties
DTU	*Danmarks Tekniske Universitet*
ECR	Elliott's Combining Rule
EoS	Equation of state
FEUP	*Faculdade de Engenharia da Universidade do Porto*
GC	Group contribution
GM	Geometric mean
HV	Huron-Vidal mixing rule
HM	Hudson-McCoubrey
LJ	Lennard-Jones
LLE	Liquid-liquid equilibrium
LSRE-LCM	Associate Laboratory Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials
MEG	Monoethylene glycol
MM	Molecular mass
mCR-1	Modified CR-1 combining rule
NRHB	Non-Random Hydrogen Bonding
NRTL	Non-Random Two-Liquid
OF	Objective function
PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
PR	Peng-Robinson
PSPs	Partial Solvation Parameters
QS	Quacquarelli Symonds
RK	Redlich-Kwong
SAFT	Statistical Associating Fluid Theory
SI	International System of Units
sCPA	Simplified Cubic Plus Association
SRK	Soave-Redlich-Kwong
TPT	Thermodynamic Perturbation Theories
UNIFAC	UNIversal quasichemical Functional group Activity Coefficients
UNIQUAC	Universal Quasichemical
VBA	Visual Basic for Applications
VLE	Vapour-liquid equilibrium
vdW	van der Waals
vdW1f	van der Waals one fluid

Chapter 1

Introduction

In the chemical industry, the processes of primary importance are the ones contemplating solids, liquids and gases with mixing, converting and separating purposes [1]. Most of them are performed near the equilibrium conditions, but, even for the ones which don't, a detailed knowledge of the equilibrium is highly required, making Thermodynamics crucially important for the safety of workers and success of enterprises.

In Denmark, in 2018, this branch of industry recorded sales of more than 6 billion euros and had more than 10 000 direct employees in 277 companies [2]. The outstanding quality of products, the strong environmental protection, the well-educated personnel and the high innovation are some of the most important characteristics of the Danish chemical industry, whereas some drawbacks related to high taxation, high labour cost, lack of competitiveness and overlegislation still exist.

On the other hand, during the same year, it represented almost 5 billion euros in Portugal, with approximately 14 000 employees in 867 different companies. The Portuguese chemical industry has very good logistics, taking advantage of the peripheral geography, the human resources have a deep know-how at reasonable costs, there are prestigious chemical engineering schools and the research and investment have been drastically increasing over the last few years. However, it fights with gaps in its value chain, nonexistence of natural gas reserves and high electricity costs [2].

In the future, chemical engineers are expected to play an important role in the production of novel materials, in decarbonising the atmosphere, in treating waste, in controlling processes, in reducing pollution, in designing products, in working at nanoscale and in further developing Biotechnology [3]. Thermodynamic properties and phase equilibria play a considerable role in these fields and, due to their accurate performance and versatility, equations of state are crucial for future developments. The Cubic Plus Association (CPA), for example, is an equation of state (EoS) which combines the Soave-Redlich-Kwong (SRK) EoS with the association term of the Wertheim theory [4], and it has been successfully applied to a wide range of systems in the chemical engineering industry, comprising mixtures with compounds such as organic acids, water, hydrocarbons [5], glycols and alcohols [6]. The proper description of these systems is really important in the chemical industry, especially to what concerns separation processes, which can account for from 40 % up to 90 % of the capital and operating costs [7].

In spite of partially solving cubic equations' limitations because of its ability to take into account hydrogen bounding [4], i.e., association, in order to do so, especially in complex phase equilibria, the CPA EoS requires some parameters and these can only be estimated from experimental data, normally from saturation pressure and liquid density data. Obviously, the big need of acquiring large amounts of data implies expensive and slow experimental procedures, often hard to perform in the majority of the companies. Besides, only a small amount of the CPA EoS parameters is known and, with the lack of experimental data, especially to what concerns electrolytes, ionic liquids, pharmaceuticals, polymers and other heavy compounds, there is a significant need of finding ways so as to be able of predicting them.

Therefore, this project intends to develop a more predictive version of the CPA EoS with the final goals of reducing the number of required parameters, of decreasing the need of undergoing experimental procedures and of allowing a better characterisation of a bigger number of systems, continuing Anders Schlaikjer's [8] and Tobias Anker Hansen's [9] previous efforts on their Master's thesis.

1.1 Problem statement

In non-associating compounds, i.e., which don't establish hydrogen bonds, the CPA EoS model gets reduced to the SRK EoS, as it will be seen later on, and requires three parameters to describe their behaviour as pure compounds. These have been shown to follow some well-defined behaviour, by chemical family, when plotted against their van der Waals volume (V_w) [9], i.e., the volume occupied by each mole of the compound, which is considered impenetrable to other molecules at ordinary temperatures [10]. This fact allows them to be easily predicted when experimental data are not available by mathematical expressions, i.e., correlations.

For the case with associating compounds, the Wertheim's theory term adds two more parameters and, this time, clear trends, i.e., common behaviours, haven't been found so far, which apparently undermines the predictive capabilities. However, Schlaikjer [8] showed that quite acceptable results can be obtained by keeping these last two constant (association parameters), calculating two of the remaining three out of correlations and fitting the last one to some experimental data, for example, liquid density data and saturation pressure data [9].

Afterwards, Hansen [9], continuing the work of Schlaikjer [8], tried to introduce partial solvation parameters (PSPs), basically a predictive version of the Hansen solubility parameters, to predict one of the CPA's association parameters, the association energy parameter, ε. In spite of, theoretically, ε being related to the energy in hydrogen bonding, a good prediction couldn't be found. Hence, Hansen [9] focused then on establishing trend equations for all the five pure compounds' parameters of the CPA EoS between a homologous series of compounds (primary alcohols, primary carboxylic acids and primary amines), using the "trend equation fitting" method. In this method, sometimes also known as "correlation between parameters" [11], the trend equations highly increased the number of parameters, so the CPA EoS parameters could be kept constant, but including the same experimental data as with the individually fitted parameters. Using MATLAB as main optimising tool, Hansen [9] concluded that the parameters could be successfully fitted using correlations for Vapour-liquid equilibrium (VLE) calculations.

In their works, both Schlaikjer [8] and Hansen [9] mentioned the Group Contribution (GC) method and the Hudson-McCoubrey combining rule but never applied them to the CPA EoS. In fact, following their suggestions for future work, this project aims to go forward in the developing of a more predictive version of the CPA EoS by finding more relations between the parameters, doing so in a broader perspective and including a bigger number of chemical compounds and properties, possibly using the two suggested approaches and reducing the need of data tables and the need of undergoing experiments for compounds of unknown properties.

1.2 Center for Energy Resources Engineering

This document is the result of a project developed on an exchange under the Erasmus+ Programme at the Center for Energy Resources Engineering (CERE), an independent research unit based at the *Danmarks Tekniske Universitet* (DTU) [12]. Being considered one of the leading research centres in Denmark, for instance, in flow assurance and petroleum geoscience, it was created in 2009 and the majority of its projects are related to applied thermodynamics, scientific computing and interface and colloid chemistry and are conducted in collaboration with companies.

On the other hand, DTU is a well-known technical university located in Kongens Lyngby, near Copenhagen, and it was founded in 1829 by Hans Christian Ørsted [13], the Danish physicist and chemist who discovered electromagnetism [14]. Nowadays, it has more than 11 000 students and 6000 employees and it was considered the 112th best university in the world by the Quacquarelli Symonds (QS) World University Rankings in 2019 [15].

1.3 Associate Laboratory LSRE-LCM

Being the result of an international cooperation, this project also involved another research unit, the Associate Laboratory Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM). It is based at the *Faculdade de Engenharia da Universidade do Porto* (FEUP), Portugal, and got the classification of associate laboratory in 2004, a few years later of becoming the outcome of a partnership between two previous well-known research centres. Its prime areas of work include adsorption and reaction processes, product engineering, thermodynamics and carbon materials.

FEUP is the biggest faculty of the University of Porto, a renowned Portuguese institution whose roots go back to the second quarter of the 19th century and which was considered the 328th best university in the world by the QS World University Rankings in 2019. Nowadays, FEUP has more than 8000 students and almost 2000 direct employees [16].

1.4 Author's contribution

All the work in which this document was built on was performed solely by the author, obviously under strong guidance and assessment of his supervisors, and it was completed either working at DTU Kemiteknik (DTU's Chemical Engineering Department) or working from home, with the latter being more preponderant in the last half of the semester due to the coronavirus pandemic. Additionally to the author's contribution, in the establishment of the databases some materials predeveloped by others were compiled and properly cited. Nevertheless, all documents, code and databases were created from scratch.

Being a modelling-centred project, there was no necessity of undergoing any laboratory experiments, even though previous experimental data were needed. Hence, it was developed using computational tools only, which will be discussed in a specific chapter.

1.5 Document's structure

After having had a first sight at the project in the Introduction, the following parts of the document will be detailed in different chapters.

In Chapter 2, **Computational tools**, all the used applications in storing, collecting and organising data, in performing calculations and in representing and discussing results will be shortly mentioned.

During Chapter 3, **State of art**, the theory behind crucial topics related to the Cubic Plus Association equation of state (CPA EoS) will be explained, the assumptions will be stated, some previous efforts will be analysed and some possible problems will be discussed in order to give the reader the proper tools and understanding required to analyse data.

Following, in Chapter 4, **Studies of dependence in pure compounds**, the data analysis will be started, in which some correlations will be studied between all the different CPA EoS parameters so as to find out the best variables and relations and therefore decrease the amount of experimental data needed.

Then, in Chapter 5, **Predicting properties in pure compounds**, the best parameter correlations will be used in the prediction of saturated vapour pressure and saturated liquid density in pure compounds with the CPA EoS. On the other hand, these results, obtained following four different methodologies, will be compared with experimental data.

Next, in Chapter 6, **Studies of dependence in binary mixtures**, some correlations will be searched for with the binary interaction parameters and with their respective exponents, following the Hudson-McCoubrey theory.

Afterwards, in Chapter 7, **Conclusions**, the main findings, discussions and final remarks of this project will be assessed.

Lastly, in Chapter 8, **Project assessment**, a short self-critique will be performed to the project, analysing the objectives' completion and presenting suggestions for future work.

Chapter 2

Computational tools

In this chapter, the computational tools used in the development of this project will be shortly referred and explained. Because of being a modelling-centred thesis, no especial experimental facilities nor laboratory protocols exist, but it can still be divided in the same three major bullets: collecting and storing data, processing data and reporting results.

In the project's first stages, there was a need of organising and storing a high number of values of parameters and properties after spending weeks searching for them in the literature, so Microsoft Excel, a mature spreadsheet developed by Microsoft in the Office suite of software, was used. Specifically, Office 365 under University of Porto's license was used. Even though it had major advantages as its appealing interface, its easy usage and its relatively big maturity in the engineering field, soon it became insufficient to organise data and to quickly find correlations between parameters and between parameters and properties.

Regarding further organisation of data, a routine was developed in Visual Basic for Applications (VBA), now a part of Microsoft Excel, to organise and format data. This relatively old programming language was also developed by Microsoft and lets the user highly expand Microsoft Excel's capabilities with its easy syntax and useful applications. So, it was particularly important as an interface database system.

Afterwards, SigmaPlot 11.0, a spreadsheet more directed to plot representation and developed by Systat Software Inc., was used. Contrarily to Microsoft Excel, it allows a faster representation of data and its graphing software makes data visualisation way easier, which is one of the reasons to be such a popular tool among scientific journals. Hence, it was used to determine all the correlations (linear and non-linear regressions) and to plot part of the graphs.

In order to continue the project, some additional accurate data were needed, a problem which ended up being surpassed with DIADEM Professional, the official database of the Design Institute for Physical Properties (DIPPR). The interface was used under CERE's licence and it supplied a considerable amount of accurate experimental data, with the theoretical correlations for liquid density and vapour pressure, the values for the critical properties and the values for the van der Waals volume and surface area being of the greatest importance for this work amongst all the variables obtained there.

However, even though further processing of data was then possible, none of the previously referred tools could perform hard calculations in a user friendly and not too time-consuming manner, so a new routine was written in VBA to export data to another program, MATLAB R2018b. This tool was used under DTU's licence and it was originally developed by MathWorks. Basically, it is a strong numerical computing environment widely used nowadays and with some powerful packages, as, for example, Simulink. In this project, MATLAB was used to perform all the predictions of properties and to plot their respective graphs. Later, the plot representation feature became even more important while studying the binary interaction parameters with the Hudson-McCoubrey theory.

Finally, OverLeaf, an open source LATEX writing interface developed by Writelatex Limited, was used to write this report. Having in mind the document's size, complexity, writing rules and abundance of figures and tables, this writing interface was undoubtedly the easiest to work with. Over the last years, it has become more popular and it is now very used amongst engineering students and researchers, majorly because of the final documents' professional appearance and unlimited customisation.

Lastly, it must be said that all documents in the different programs were started from scratch and that each interface required some skill learning / improving.

Chapter 3

State of the art

Throughout this chapter, a literature review will be performed, minutely explaining the most important concepts related to the Cubic Plus Association equation of state. Further, the most important assumptions will be stated in each section and some problems will be anticipated.

3.1 Thermodynamics and equations of state

By definition, Thermodynamics is the physical science which studies the relationship between energy and work as well as the equilibrium states and variables of systems [17]. The most important concept in this branch of science is considered to be the one of state, so the full characterisation of the properties of a system. Since it is impossible to completely determine the microscopic state of all the particles (masses, velocities, positions, etc), they are studied from a macroscopic point of view, making usage of the equations of state.

An equation of state (EoS) is a mathematical equation which relates the state variables of a system, for example, temperature, pressure and volume. In the chemical and oil industries, they are, normally, either based on the virial coefficients or based on the cubic van der Waals (vdW) equation of state [18].

The most well-known virial-derived equations are the Benedict–Webb–Rubin EoS [19], the Bender EoS [20] and the Lee–Kesler EoS improved by Plöckner [21]. To what concerns cubic equations of state, which will be studied in detail in the next section, the most common are the van der Waals EoS, the Redlich-Kwong (RK) EoS, the Soave-Redlich-Kwong (SRK) EoS [22] and the Peng-Robinson (PR) EoS [23].

3.2 Cubic equations of state

The cubic equations of state, widely used in the oil industry, were named this way since the determination of the molar volume as a function of temperature and pressure when using them requires solving a third-degree equation [18]. Like with all scientific methods, their usage has some advantages and some drawbacks. The most important advantages consist in the simplicity of the cubic EoS, in their wide applicability range of temperatures and pressures, in being accurate at describing both liquid and vapour phases and in having sufficient experimental data and correlations available [4]. In opposition to that, the calculations can be too sensitive to small changes in the parameters, they do not properly predict the liquid volume and the vapour pressures can be very sensitive to the critical properties [4].

The first of its kind was put forward by van der Waals in the 19th century and had two terms, as it can be seen in equation 3.1.

$$P = \frac{R_{\mathrm{g}}T}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2} \tag{3.1}$$

Where P is the pressure, R_{g} is the ideal gas constant, T is the temperature, V_{m} is the molar volume, b is the co-volume and a is the energy parameter.

As observed above, the first term would express the Ideal Gas Law if the co-volume was equal to zero. Moreover, when the pressure goes to infinity, V_{m} becomes equal to b [18]. The second term, non-existent on the Ideal Gas Law, accounts for the intermolecular attraction, which seems logic when it is noticed that it is proportional to the square of the molar concentration.

Still, some other equations exist, as the one developed by Soave [22], which will be studied in the next subsection, and the one by Peng and Robinson, the so called Peng-Robinson equation (PR) [23], normally written in the form of equation 3.2.

$$P = \frac{R_{\mathrm{g}}T}{V_{\mathrm{m}} - b} - \frac{a(T)}{V_{\mathrm{m}}^2 + 2V_{\mathrm{m}}b - b^2} \tag{3.2}$$

Where *a(T)* highlights the fact that the energy parameter is now considered to be a function of temperature.

The PR EoS has two important differences when compared to equation 3.1, being the first one considering the energy parameter a function of the temperature, as already mentioned, and the second one the form of the intermolecular attraction term, which started to have in consideration both a and b.

3.2.1 Soave-Redlich-Kwong equation of state

Regarding the fact that the Soave-Redlich-Kwong (SRK) EoS is the only one which will be used later on, since it is the basis of the CPA EoS, a specific subsection was thought on. This equation was proposed by Soave as an adapted Redlich-Kwong (RK) EoS and, for pure compounds, can be written in terms of pressure as equation 3.3 shows.

$$P = \frac{R_{\mathrm{g}}T}{V_{\mathrm{m}} - b} - \frac{a(T)}{V_{\mathrm{m}}(V_{\mathrm{m}} + b)} \tag{3.3}$$

As previously seen, b refers to the co-volume parameter and can be determined by equation 3.4 [9].

$$b = 0.08664\frac{R_{\mathrm{g}}T_{\mathrm{c}}}{P_{\mathrm{c}}} \tag{3.4}$$

Where T_{c} is the critical temperature and P_{c} the critical pressure.

Besides, the only difference between the SRK EoS and the RK EoS is the specific temperature dependency of a, which, in the corrected one, is given by equation 3.5 [9].

$$a(T) = a_0\left[1 + c_1(1 - \sqrt{T_{\mathrm{r}}})\right]^2 \tag{3.5}$$

Where T_r is the reduced temperature and a_0 and c_1 are parameters which account for the temperature dependency of the energy parameter and are normally called energy term parameters. They are calculated by equations 3.6 and 3.7, respectively, for the pure SRK EoS.

$$a_0 = 0.42748\frac{(R_\mathrm{g}T_\mathrm{c})^2}{P_\mathrm{c}} \tag{3.6}$$

$$c_1 = 0.48 + 1.574\omega - 0.176\omega^2 \tag{3.7}$$

Where ω, first introduced by Pitzer *et al.* [24], is called the acentric factor.

Finally, it must be said that equations 3.4, 3.6 and 3.7 are only valid for the SRK EoS and under especial circumstances, since they are the result of correlations performed for some non-associating compounds, like regular alkanes. On the other hand, equation 3.5 is theoretically-based and will be later used in the CPA EoS.

3.2.2 Mixing rules

As referred to in the previous subsection, the SRK EoS and all the cubic EoS, in general, were developed for pure compounds. Therefore, they often fail to describe the properties of a mixture of compounds even though they can correctly predict the behaviour of each compound separately. Being so, in order to successfully apply them to mixtures, mixing rules must always be used. Some of the most well-studied are the Huron-Vidal (HV) mixing rule, the Wond-Sandler mixing rule and the van der Waals one fluid mixing rules (vdW1f) [4].

The Huron-Vidal mixing rule [25] was the first successful effort in developing an EoS/G^E, i.e., a specific kind of mixing rules that puts together a cubic EoS and an activity coefficients model [4]. This last term makes usage of the excess Gibbs energy, G^E, to dictate the mixing rules of, typically, the energy parameter, a.

The normal starting point to conceive an EoS/G^E model is to equal the excess Gibbs energies of the applied equation of state (vdW EoS, SRK EoS, PR EoS, etc) and the chosen activity coefficient model at a reference pressure, P, as equation 3.8 shows [4].

$$\left(\frac{g^\mathrm{E}}{R_\mathrm{g}T}\right)_P^\mathrm{EoS} = \left(\frac{g^\mathrm{E}}{R_\mathrm{g}T}\right)_P^\mathrm{model} \tag{3.8}$$

Where the reference pressure, P, is commonly considered to be infinite, for example, in the HV and Wong–Sandler models, and zero in some other models. On the other hand, g^E stands for the molar excess Gibbs free energy.

By looking at equation 3.3 and using the Soave-Redlich-Kwong EoS as an example, it can be seen that when pressure, P, goes to infinity, ∞, the denominator of the first right hand side term becomes zero, i.e., V_m approaches the co-volume parameter, b, in which the linear mixing rule of equation 3.9 is assumed.

$$b = \sum_i x_i b_i \tag{3.9}$$

Originally, the Huron-Vidal mixing rules were employed to the SRK EoS and to the Non-Random Two-Liquid (NRTL) model, but later their application was extended to all types of equations based on the vdW EoS [4]. In general, the HV mixing rules offer more flexibility and accuracy over the vdW1f mixing rules for mixtures of polar and associating compounds. However, a crucial limitation of the HV mixing rules is the impossibility of using large collections of data derived from models such as Wilson, UNIversal quasichemical Functional group Activity Coefficients (UNIFAC) and Universal Quasichemical (UNIQUAC), which are based on low-pressure data.

This way, taking the same path Hansen [9] took in his master's thesis, a good alternative would be the van der Waals one fluid mixing rules. The vdW1f are very popular amongst the oil and gas industries and their application is limited to non-polar compounds, frequently being unable to describe the behaviour of highly non-ideal mixtures [26].

Following the vdW1f mixing rules, the overall energy parameter for the mixture, a, is determined by equation 3.10 [26].

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3.10}$$

Where a_{ij}, a sort of average energy parameter and usually called cross energy parameter, can be determined by the classic combining rule of equation 3.11.

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{3.11}$$

Equation 3.11 is frequently referred to as the geometric mean (GM) of the energy parameters.

With a similar logic, the co-volume parameter can be calculated by equation 3.12.

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{3.12}$$

Where b_{ij}, the cross co-volume, can as well be determined by different combining rules. The most common approach, though, calculates an arithmetic mean (AM), assuming the form of the equation 3.13 [27].

$$b_{ij} = \frac{b_i + b_j}{2} \tag{3.13}$$

In spite of not being used in this project, it should be known that the classic combining rule uses an GM instead of a AM as the mixing rule for the co-volume [28].

The binary interaction parameter k_{ij} is an adjustable constant normally obtained from experimental phase equilibrium data [9]. The indices i and j in equations 3.10, 3.11, 3.12 and 3.13 refer to all the compounds present in the mixture, so all the different possible combinations are taken into account.

3.3 Association and associating compounds

The cubic EoS are unable of properly describing the behaviour of mixtures with highly polar and/or strongly associating compounds [4], i.e., compounds which establish hydrogen bonds, because of the relatively large energy involved [9]. Some compounds known for their strong associating properties are water, amines, acids, alcohols and phenols [4].

To the ones which are capable of creating hydrogen bonds with species of their own kind, like in the case of water, it is said they are self-associating compounds or that are capable of self-association. To the other species, which may associate with compounds of other kinds, it is said they are cross-associating or can undergo cross-association. Basically, all associating compounds can be cross-associating but only a fraction of them can self-associate.

3.3.1 Association theories

Lately, many association theories have been coupled to EoS so as to account for the hydrogen bonds' energy, and they can be roughly divided into three different groups: chemical theories, lattice–fluid theories and perturbation theories. These models are, generally, non-cubic EoS and have several additive contributions which account for attractive van der Waals forces and association phenomena [29].

The chemical theories are based on the quantification of new species formation and take into consideration the amount of products formed as a function of temperature, composition, association strength and density [9]. Moreover, the equilibrium constants are fitted to experimental data and are adjustable parameters. In the early stages, these kind of theories used to be expressed in the form of activity coefficient models, but, nowadays, the most widely spread chemical EoS categories are those having a non-cubic physical term and those for which cubic EoS are used in the physical part [4]. One good example of a chemical theory is the Associated Perturbed Anisotropic Chain Theory (APACT), which has five different parameters normally fitted to the experimental data [30].

Lattice-fluid theories, or quasi-chemical theories, on the other hand, are based on the number of new bonds formed between molecules which occupy adjacent sites, i.e., hydrogen bonding sites, in a lattice [29]. The Non-Random Hydrogen Bonding theory, also known as NRHB, is a pretty good example of a compressible lattice model, where the density variation caused by temperature and pressure changes is taken into account by the usage of holes, i.e., not occupied lattices, and having in consideration the non-random distribution of molecular sites [31].

Finally, the Thermodynamic Perturbation Theories (TPT), which require solving integral equations using a potential function, have found a huge application in different areas of interest, with the most well-studied being the Statistical Associating Fluid Theory (SAFT) EoS and the Cubic Plus Association (CPA) EoS. The term "perturbation" refers to the method of using an expansion to determine an approximate expression from a known related one [8] and these type of theories calculate the energy which results from hydrogen bonding by statistical mechanics [9].

3.3.2 Wertheim's association theory for the CPA EoS

Several association models have been developed to describe the behaviour of highly polar mixtures, being two of the most popular the chemical theory, already mentioned, and the Wertheim's association theory [32].

The Wertheim's association theory, which is based on the perturbation theory, was firstly developed by Michael S. Wertheim [33] and it is an important part of both the SAFT EoS and the CPA EoS [8]. It calculates the probability of formation of a complex, i.e., the result of an interaction between two different sites [32], and it is especially good when applied to non-spherical chain fluids [33].

Originally, the Wertheim's association term was presented, in terms of the compressibility factor of association, $Z^{\text{association}}$, as equation 3.14 shows [34], but later it was modified by Michelsen *et al.* [35] in order to ease calculations and computer simulations, presenting the form of equation 3.15 and being the only one used nowadays.

$$Z^{\text{association}} = \left(\frac{PV_{\text{m}}}{R_{\text{g}}T}\right)^{\text{association}} = \rho\sum_i x_i \sum_j x_j \sum_{A_i}\left[\left(\frac{1}{X_{A_i}} - \frac{1}{2}\right)\frac{\partial X_{A_i}}{\partial \rho_i}\right] \tag{3.14}$$

Where $Z^{\text{association}}$ is the compressibility factor of association, ρ is the molar density, x_i and x_j are the molar fractions of the i^{th} and j^{th} components, A_i is a hydrogen bonding site on a molecule i and X_{A_i} is the fraction of site A in a i molecule which are not bounded to other active sites.

$$Z^{\text{association}} = -\frac{1}{2}\left(1+\rho\frac{\partial g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1-X_{A_i}) \tag{3.15}$$

Where g is the radial distribution function, which can be obtained from the simplified equation 3.16 proposed by Kontogeorgis *et al.* [36] and Elliott *et al.* [37].

$$g(\rho) = \frac{1}{1-\frac{1.9}{4}b\rho} \tag{3.16}$$

In equation 3.15, the summations should be performed over all bonding sites and for all components [9]. The terminology of bonding sites and association schemes, i.e., the number and type of association sites [4], follows what Huang *et al.* [38] proposed, so X_{A_i} can be calculated using equation 3.17.

$$X_{A_i} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{B_j}\Delta_{A_iB_j}} \tag{3.17}$$

Where B stands for a different type of association sites and $\Delta_{A_iB_j}$ for the association strength, calculated by equation 3.18 in the CPA EoS.

$$\Delta_{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{R_{\text{g}}T}\right)-1\right]b_{ij}\beta^{A_iB_j} \tag{3.18}$$

Where $\varepsilon^{A_iB_j}$ is the cross-association energy parameter and $\beta^{A_iB_j}$ is the cross-association volume parameter [39], both usually obtained from experimental data. From this point on, their superscripts will be omitted for the sake of simplicity and the parameters will only be referred to as ε and β, respectively.

This last equation was based on the Elliott's combining rule. Following, the combining rules will be deeper studied.

3.3.3 Combining rules

Although no mixing rules are required in the Wertheim's association theory [4], the same can't be stated about combining rules. Whenever dealing with a mixture of two associating compounds, for example, n-pentanol and water, some combining rules are demanded for the earlier studied parameters, ε and β, so one is able of properly calculating the association strength which characterises the system.

Firstly, the association strength of the two combined chemical compounds can be given by equation 3.19, known as the Elliott's Combining Rule (ECR). In its microscopical essence, it presupposes that the strength of association between two different sites (*A*/*B*) in two different particles is given by the GM of the association strength they would establish between themselves and a different association site in the same molecule.

$$\Delta_{A_iB_j} = \sqrt{\Delta_{A_iB_i}\Delta_{A_jB_j}} \tag{3.19}$$

Where $\Delta_{A_iB_i}$ is the association strength between association sites A and B in an i molecule and $\Delta_{A_jB_j}$ is the association strength between association sites A and B in a j molecule.

Commonly, the cross-association energy, ε, is calculated by equation 3.20, using the so called combining rule 1 or CR-1, for short, which is simply an AM of the chemical species' association energies. The ECR uses the same expression to calculate the cross-association energy.

$$\varepsilon = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \tag{3.20}$$

On the other hand, the cross-association volume parameter, β, is given by equation 3.21 [40], which also constitutes the CR-1 rule.

$$\beta = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \tag{3.21}$$

After performing two approximations in equation 3.18, $g(\rho) \cong 1$ and $\exp(\frac{\varepsilon^{A_iB_j}}{R_gT}) - 1 \cong \exp(\frac{\varepsilon^{A_iB_j}}{R_gT})$, the equivalent expression can be obtained for the cross-association volume with the ECR, equation 3.22 [4].

$$\beta = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}}\,\frac{\sqrt{b_ib_j}}{b_{ij}} \tag{3.22}$$

The ECR and the CR-1 rules are, in fact, very similar and both the rules have been found successful and present a characteristic advantage: the AM for the cross-association energy, ε, is related to the enthalpy of hydrogen bonding and the GM for the cross-association volume, β, is also related to the cross-entropy of the hydrogen bonding [4].

Nevertheless, in the presence of systems where solvation, i.e., cross-association, may happen, a modified CR-1 rule, mCR-1, is most often used. These mixtures, usually called "solvating mixtures", have in their composition one self-associating and one inert compound. When using the mCR-1 rule, the cross-association volume parameter is no longer calculated, but fitted to experimental data, and the cross-association energy parameter is obtained by dividing by two the value of the associating compound, equation 3.23, since the association energy of the inert compound is zero [4].

$$\varepsilon = \frac{\varepsilon_{\text{associating}}}{2} \tag{3.23}$$

Some of the most common solvating systems are water with ethers, water with aromatic hydrocarbons and glycols with aromatic hydrocarbons.

3.4 Cubic Plus Association equation of state

After reading the two previous sections, the five different model parameters used in the Cubic Plus Association EoS should be known: a_0, b and c_1, which derived from the SRK EoS and from the mixing rules, and ε and β, which appeared in the Wertheim's association term and derived from the combining rules.

As it can be seen in equation 3.24, the first three parameters appear in the first and second terms of the CPA EoS and the last two only in the third one.

$$P = \frac{R_g T}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{R_g T}{V_m}\left[1 + \frac{1}{V_m}\frac{\partial \ln g(\rho)}{\partial \rho})\right]\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \tag{3.24}$$

Actually, the version of the CPA EoS presented by equation 3.24 is normally called simplified Cubic Plus Association (sCPA) EoS, since it is the result of two important simplifications stated before [8]: having used the association term in the form proposed by Michelsen *et al.* [35] and having used the radial function suggested by Kontogeorgis *et al.* [36] and Elliott *et al.* [37] in their studies.

Furthermore, this equation puts together two other expressions which were already mentioned. The first term is the SRK equation of state, equation 3.3, and the remaining one is the Wertheim's association term, equation 3.15, written in terms of pressure. Whenever in the presence of a non-associating compound, the associating term becomes zero, so only the parameters a_0, b and c_1 are needed. In the CPA EoS, the parameters a_0, b and c_1, together with the associating parameters ε and β, are fitted to experimental data and not calculated from correlations as in the SRK EoS. The energy parameter, a, accounts for the van der Waals interactions between molecules. On the other hand, a_0 and c_1 are empirical constants which establish the temperature dependence of the energy parameter. Sometimes, in order to avoid ambiguities, the a_0 parameter is presented in a corrected form as Γ, as equation 3.25 shows [41].

$$\Gamma = \frac{a_0}{R_g b} \tag{3.25}$$

The co-volume parameter, b, refers to the space physically occupied by the molecules in a specific volume. It can be easily calculated if the free volume is subtracted from the total volume. In fact, both a and b quantify the deviation of the compound or mixture to which the model is being applied to from the reference fluid, i.e., an ideal gas [42]. For the energy parameter, the vdW1f mixing rules will be used, traduced by equations 3.10 and 3.11, where the cross energy parameter derives from a GM. On the other hand, a simple AM will be considered for the cross-covolume, as equations 3.12 and 3.13 have shown.

As previously referred to, one CPA EoS interaction parameter, k_{ij}, accounts for corrections in the mean rule of the energy parameter [4], a. Originally, it was determined from fitting Vapour-liquid equilibrium (VLE) experimental data at a specific temperature and extrapolated for the remaining temperatures of interest [43], but nowadays some other methods have emerged.

Finally, the association parameters, ε and β, are related to the bonding strength of two sites. The association energy, ε, refers to the energy of association itself and the product $b \cdot \beta$ is the volume of association [9], which is useful to measure the dimension of the association. Both ε and β can be considered pure compounds' parameters whenever in the presence of self-associating compounds, since they are able to establish association with molecules of the same species. As early stated, these two parameters are, generally speaking, obtained as well from fitting the model to experimental data, normally saturation pressure and liquid density data, and, in solvating mixtures, normally the mCR-1 rules are considered.

3.4.1 Comparing the CPA EoS with the PC-SAFT EoS

Now that a version of the CPA EoS was fully presented, a comparison with the most used version of the SAFT EoS model, the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EoS, will be performed in this section, since they are two widely used equations of state.

The SAFT family EoS are theoretically derived models, which are based on the perturbation theory. Essentially, the majority of the variations of the SAFT EoS have a different approach of the dispersion term. The main change in the PC-SAFT EoS when compared to the SAFT EoS is the fact of taking a reference system of hard-sphere chains so as to attempt the modelling of asymmetric and highly non-ideal mixtures, which, in the end, makes calculations much simpler [8]. Specifically, the dispersion term in PC-SAFT only accounts for dispersion between whole chains.

The PC-SAFT EoS and the CPA EoS are the two most used models applied to describe, for instance, aslphaltene precipitation, and both have a physical part and an association part in their main equations [42]. The physical part in the CPA EoS is described by a cubic EoS and the physical part of the PC-SAFT EoS is based on the Wertheim's first order TPT. Their association terms, however, are both based on the Wertheim's association term.

The PC-SAFT EoS, similarly to the CPA EoS, requires three pure component parameters for non-associating compounds and has been useful describing the behaviour of complex phase equilibrium systems, like polymers and their mixtures, water and electrolytes and surfactant and micellar systems [44]. However, the parameters used in the PC-SAFT EoS have a very specific physical meaning, like the length and diameter of the segment being studied, while the parameters in the CPA EoS are more related to ideal behaviour deviance, which is not so intelligible [42].

In the oil and gas industries, a big concern about the PC-SAFT EoS is the computing time required for calculations, being this a very relevant reason for the cubic EoS still being used nowadays [42] together with their simplicity and relatively good accuracy. However, since the association term is the same, the computing time for the CPA EoS and for the PC-SAFT EoS is very similar. To what concerns their accuracy in predicting the behaviour of mixtures, it can be said that it strongly depends on the system, so sometimes the CPA EoS provides better results [45] and sometimes it is the PC-SAFT EoS [42]. It must also be taken into consideration that the quality of the fitting of the pure compounds parameters greatly affects the performance of both the models.

3.5 Hudson-McCoubrey combining rules

Following the suggestions of Schlaikjer [8] and Hansen [9], the combining rules of the Hudson-McCoubrey (HM) theory will be studied and applied.

As previously stated, the performance of the equations of state is highly influenced by the chosen mixing and combining rules. In especial, the interaction parameters in the cubic equations of state are very affected by them. Having in mind that this is particularly important to what concerns the cross-energy parameter, studying combining rules based on the theory of intermolecular forces is a must [4].

Some decades ago, Reed [46] showed that the usual combining rules could be improved in the intermolecular attraction potential by accounting for differences in the ionisation potential, i.e., the energy required to remove the most exterior electron of a chemical compound, and molar volume of the components. A few years later, Hudson *et al.* [47] reformulated his equations using the Lennard-Jones 12:6 potential and based on the London theory of dispersion. To calculate the unlike energy parameter between two central molecules, ε_{ij}, Hudson *et al.* [47] proposed equation 3.26.

$$\varepsilon_{ij} = \frac{2\sqrt{I_i I_j}}{I_i + I_j} \left[\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_{ij}} \right]^6 \sqrt{\varepsilon_i^{\mathrm{LJ}} \varepsilon_j^{\mathrm{LJ}}} \tag{3.26}$$

Where I is the ionisation potential, $\varepsilon^{\mathrm{LJ}}$ is the depth of the potential well or energy parameter, σ is the collision diameter or size parameter and σ_{ij} is the unlike size parameter, which can be calculated by the Lorentz combining rule (AM) given by equation 3.27. The indices *i* and *j* refer to all the possible combinations between the molecules *i* and *j*.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{3.27}$$

Additionally, the binary interaction parameter k_{ij} can be calculated by equation 3.28 [41].

$$k_{ij} = 1 - \frac{2^7 \sqrt{I_i I_j}}{I_i + I_j} \left[\frac{\sqrt{\sigma_i \sigma_j}}{\sigma_i + \sigma_j} \right]^6 \quad , \quad 0 \leqslant k_{ij} \leqslant 1 \tag{3.28}$$

As it could be noticed, these equations don't include the CPA EoS parameters. However, equation 3.28 can be easily converted into equation 3.29 if two approximate relations are introduced: $\varepsilon^{\mathrm{LJ}} \propto a$ and $\sigma^3 \propto b$ [9].

$$k_{ij} = 1 - \frac{2\sqrt{I_i I_j}}{I_i + I_j} \left[\frac{\sqrt{b_i b_j}}{b_{ij}} \right] \tag{3.29}$$

Lastly, and using the same relations from which equation 3.29 was derived, a_{ij} may be calculated by equation 3.30 [9].

$$a_{ij} = \sqrt{a_i a_j} \left[\frac{\sqrt{b_i b_j}}{b_{ij}} \right] \frac{2\sqrt{I_i I_j}}{I_i + I_j} \tag{3.30}$$

However, if the Lennard-Jones 12:6 potential is not considered, and a more general approach is taken, the binary interaction parameter would be calculated by equation 3.31.

$$k_{ij} = 1 - \frac{2\sqrt{I_i I_j}}{I_i + I_j} \left[\frac{\sqrt{b_i b_j}}{b_{ij}} \right]^{n/3-1} \tag{3.31}$$

Where n is an adjustable exponent normally obtained from potential functions or fitted to experimental data.

In practical terms, this means that n will be obtained from the literature values of k_{ij} instead of being considered equal to six, which is the Lennard-Jones (LJ) value. Intelligibly, if, on the other hand, the objective was to calculate the exponents n from known binary interaction parameters, equation 3.29 would have to be rearranged into equation 3.31.

$$n = 3\frac{\ln\left[\frac{(1-k_{ij})(I_1+I_2)}{2\sqrt{I_1 I_2}}\right]}{\ln\left[\frac{\sqrt{b_i b_j}}{b_{ij}}\right]} + 3 \tag{3.32}$$

Where ln() is the natural logarithm

Yet, this method of calculating the parameters requires the knowledge of the ionisation potentials for all the species present, which is often impossible. Hence, a good approximation was developed by Coutinho *et al.* [27,48] between the ionisation potentials and the co-volume of the species based on equation 3.33 [4].

$$I \propto \frac{1}{b} \Longrightarrow \frac{2\sqrt{I_i I_j}}{I_i + I_j} \cong \left(\frac{\sqrt{b_i b_j}}{b_{ij}}\right)^{-1} \tag{3.33}$$

This way, the previous equation leads to an alternative method of determining k_{ij} when replaced in equation 3.31, equation 3.34.

$$k_{ij} = 1 - \left(\frac{\sqrt{b_i b_j}}{b_{ij}}\right)^{n/3-2} \tag{3.34}$$

Which implies that the exponents n are given by equation 3.35.

$$n = 3\frac{\ln(1-k_{ij})}{\ln\left[\frac{\sqrt{b_i b_j}}{b_{ij}}\right]} + 6 \tag{3.35}$$

Where ln() is the natural logarithm.

3.6 Group contribution theory

Similarly to the Hudson-McCoubrey combining rules, some group contribution (GC) methods will be discussed as Schlaikjer [8] and Hansen [9] suggested.

Despite all the available methods of performing parameter estimation in cubic equations of state, the most widely applied one makes usage of critical properties, which, when not available, can be estimated with group contribution methods [4]. The Group Contribution (GC) methods rely on the additive principle, in which each molecule is divided into fragments, usually atoms, bonds or groups of atoms [49]. These fragments are considered to have a partial value of the whole molecule property, called a contribution, and they are normally known from experimental data. Hence, the property of the molecule is the property of the compound itself and is obtained by summing all the contributions.

Mainly over the last century, a considerable amount of contribution methods and theories have been developed with the aim of predicting different properties, such as the critical properties (Lydersen [50], Joback *et al.* [51]), the parameters of equations of state (Constantinou *et al.* [52]), the activity coefficients, the vapour pressure, the liquid viscosity and density, the gas viscosity, the heat capacity, the surface tension, the normal boiling temperature and the van der Waals volume (Bondi [53]) [49].

A particularly successful group-contribution method was developed by Marrero *et al.* in 2001 [54] which considered three levels of contributions. In the primary one, simple groups are used to describe a big variety of organic compounds, while in the second and third levels, also known as higher levels, polyfunctional and structural groups allow a better characterisation of some molecular fragments [54].

Looking, for example, at the chemical structure of 1-phenylethanone, a solvent and flavouring agent, Fig. 3.1, it is possible to perform a division in seven simple primary groups: five aromatic carbons bonded to one atom of hydrogen each in red (- -), one aromatic carbon bonded to a carbonyl group in blue (-··-) and a methyl group in green (-···-) [54].

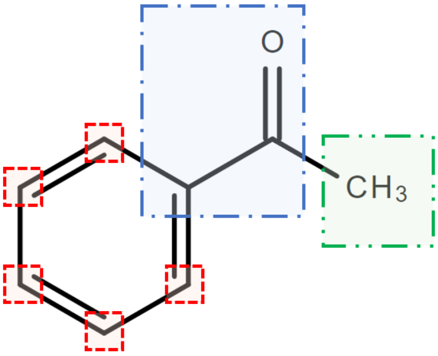

Fig. 3.1: 1-phenylethanone chemical structure and respective division in first-order groups. Reprinted and adapted from [55].

As stated before, if a *W* property was being calculated for this chemical compound and based on the Marrero *et al.* [54] method, it would be the result of the sum of the contributions of all the groups, with the overall calculation performed by equation 3.36.

$$f(W) = \sum_i N_i C_i + \Omega \sum_j N_j M_j + \zeta \sum_k N_k E_k \tag{3.36}$$

Where *f(W)* is a function of the target property W, N_i is the number of existent i groups, C_i is the contribution of the first-order group of type i, N_j is the number of existent j groups, M_j is the contribution of the second-order group of type j, N_k is the number of existent k groups, E_k is the contribution of the third-order group of type k and Ω and ζ are weighting factors which take the value of zero or one depending on the level of estimation.

Whether considered that no higher levels estimations were needed for the case of 1-phenylethanone, Ω and ζ would be both zero and W would be given by the simplified equation 3.37.

$$f(W) = 5 \cdot C_1 + 1 \cdot C_2 + 1 \cdot C_3 \tag{3.37}$$

Where C_1 is the contribution of an aromatic carbon bonded to an atom of hydrogen, C_2 is the contribution of an aromatic carbon bonded to a carbonyl group and C_3 is the contribution of one methyl group.

3.6.1 Bondi's method

The van der Waals volume, i.e., the volume occupied by each mole of the compound, which is considered impenetrable to other molecules with thermal energies at ordinary temperatures [10], had a proven key role in the fitting of CPA EoS parameters [9], as previously mentioned.

A very straightforward method of calculating it relies on the Bondi's group contribution method, which considers the volume occupied by a molecule function of the bond distances, l_d, of the bond angles, of the characteristic shapes of the atoms in various configurations and of the intermolecular van der Waals radius, r_w, i.e., the non-bonded contact radius [53]. This method also allows the determination of the van der Waals surface area.

Fundamentally, it supposes that the atoms have spherical shapes and considers that the van der Waals radius is constant, regardless of the chemical combination, chemical nature of the mixture and phase state. These assumptions are valid for heavy molecules but they are not so precise for light atoms such as hydrogen or fluorine. Additionally, it was noticed that, when in the presence of strong association, the participating atoms may suffer sufficient deformation to make radii calculations harder [53].

Going back to the example of 1-phenylethanone and remembering its chemical structure, Fig. 3.1, Bondi's method can be applied to determine both van der Waals volume, V_w, and van der Waals surface area, A_w. Firstly, it must be known that all the previously identified groups have an individual contribution Q for the relative molecular surface area q and an individual contribution R for the relative molecular volume r. Secondly, so as to determine the stated molecule properties, all the contributions need to be summed, following equations 3.38 and 3.39, respectively.

$$q = \sum_i N_i Q_i \tag{3.38}$$

$$r = \sum_i N_i R_i \tag{3.39}$$

Where q is the relative van der Waals molecular surface area, N_i is the number of groups i, Q_i is the i group's relative van der Waals molecular surface area contribution, r is the relative van der Waals molecular volume and R_i is the i group's relative van der Waals molecular volume contribution.

Finally, to obtain A_w and V_w, equations 3.40 and 3.41 must be used, respectively, in which q and r are multiplied by normalisation factors related to a methylene unit in polyethylene [56].

$$A_\text{w} = 2.5 \cdot 10^9 \cdot q \tag{3.40}$$

$$V_\text{w} = 15.17 \cdot r \tag{3.41}$$

In the Dortmund Data Bank [57], a table was found with R's and Q's, which is available in Appendix B.

For the case of 1-phenylethanone, A_w and V_w can be obtained by substituting values on the last four equations and achieving equations 3.42 and 3.43, respectively.

$$A_\mathrm{w} = 2.5 \cdot 10^9 \cdot [5 \cdot 0.4000 + 1 \cdot 0.8400 + 1 \cdot 0.8480] = 9.22 \cdot 10^9\ \mathrm{cm}^2 \cdot \mathrm{mol}^{-1} \tag{3.42}$$

$$V_\mathrm{w} = 15.17 \cdot [5 \cdot 0.5313 + 1 \cdot 1.1358 + 1 \cdot 0.9011] = 71.20\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \tag{3.43}$$

Another easy example is 3-pentanone, a popular solvent in the paint industry, and its chemical structure and division in groups can be observed in Fig. 3.2.

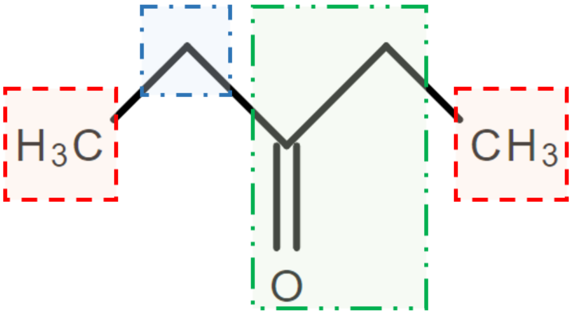

Fig. 3.2: 3-pentanone chemical structure and respective division in first-order groups. Reprinted and adapted from [58].

This way, the molecule was divided in four different primary groups: two methyl groups in red (**- -**), one methylene group in blue (**-**··**-**) and one carbonyl group bonded to an ethylene group in green (**-**···**-**).

After consulting Appendix B, the van der Waals surface area and volume can be given, respectively, by equations 3.44 and 3.45.

$$A_\mathrm{w} = 2.5 \cdot 10^9 \cdot [2 \cdot 0.8480 + 1 \cdot 0.8400 + 1 \cdot 1.1800] = 8.5 \cdot 10^9\ \mathrm{cm}^2 \cdot \mathrm{mol}^{-1} \tag{3.44}$$

$$V_\mathrm{w} = 15.17 \cdot [2 \cdot 0.9011 + 1 \cdot 1.1358 + 1 \cdot 1.4457] = 59.50\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \tag{3.45}$$

3.7 Previous efforts on predictive models

In this section, a small analysis will be performed on previous efforts of developing a more predictive CPA EoS, including the ones of Schlaikjer [8] and Hansen [9].

One approach to a more predictive model was performed by Palma *et al.* [59], who modified the sCPA EoS using a version of the Mathias-Copeman $a(T)$ function and a simplified radial distribution function so as to enhance prediction accuracy. In specific, the used version of the CPA EoS forced the correct determination of the critical properties (T_c and P_c) and of all the properties which depend on them, such as the heat of vaporisation. Moreover, well-defined tendencies were reported for the energy and co-volume parameters with the van der Waals volume for a set of compounds, mainly alcohols and diols, as it can be seen in Fig. A.1 in Appendix A, and for the binary interaction parameter k_{ij} with the molecular mass, i.e., chain length, for monoethylene glycol (MEG) and light alkanes systems.

Remarkably, the predictive capacity of the model was increased since all the results were obtained with a constant and transferable value for the association energy parameter of the hydroxyl group and with an increase in simplicity in the handling of the association volume [59]. The results were very similar to the ones from the pure sCPA EoS in binary and multicomponent system calculations, despite the binary interaction parameters k_{ij} were higher. Additionally, even though the total number of analysed compounds and chemical families was relatively small, it can be said, rather safely, that exists a good relation between the energy and co-volume parameters with the van der Waals volume.

Schlaikjer [8] also studied the correlation between the co-volume and the van der Waals volume, having obtained the equation $b = 0.000179 \cdot V_{\mathrm{m}} - 0.01332$ and a coefficient of determination of 0.9918 for the linear fit of compounds including alkanols, alkanes, esters, ethers, glycols, ketones and phenols, as Fig. A.2 in the appendices illustrates. The ability of establishing a linear relationship between these two variables, even accounting for compounds of different chemical families, gives a good indication of the possibility of going further in the predictiveness of the CPA EoS model. So, if a proper equation (this or another) is found to completely correlate the co-volume and the van der Waals volume, one less parameter would be needed.

Moreover, Schlaikjer [8] repeated the procedure for both the energy term parameters, a_0 and c_1, but only the former showed satisfactory results. In fact, a good second degree relationship was found between the energy parameter and the van der Waals volume, as Fig. A.3 in the appendices illustrates, with a determination coefficient of 0.9938. When analysed in more detail, it can be noticed that the part of the data with fluorine-containing compounds was ignored in the second degree fit, as Fig. A.4 shows. Being so, more extensive studies need to be undergone in order to understand the variation in this family and conclude about the validity of the fit for a more predictive version of the CPA EoS. Nevertheless, with the exception of this family of compounds, the outcome seems reasonably good, so there might be a chance of going further in the predictive capabilities.

Besides, Schlaikjer [8] noticed that the energy term parameter, c_1, had a regular behaviour in compounds of the same chemical family, presenting some reasonable second degree correlations, even though only a few compounds of each family were analysed, with the exception of n-alkanes, which had a more significant sample, as Fig. A.5 shows. Consequently, more compounds need to be added to the database so a more accurate common behaviour can be found within a chemical family. Moreover, in his studies, Schlaikjer [8] tried and managed to find some relations between the interaction parameter k_{ij} and the carbon number in alkanes. Alkanes vary in a constant way as the number of carbons increase in their molecular structure, apparently allowing to easily characterise and predict the parameters within their family. Taking advantage of this fact and applying it to some other families, the two association parameters were obtained from the geometric means of all the values in the chemical family and kept constant for all compounds, while two of the remaining three were calculated from correlations and the last one was fitted to experimental data, with results even more accurate than fitting all five parameters to experimental saturation pressure and liquid density data being reported [9]. In his Master's thesis, Ali [60] noticed exactly the same behaviour and also found a very well-defined trend in the energy term parameter, c_1, with the molecular mass (MM) of hydrocarbons, as Fig. A.6 shows.

Besides this, Ali [60] also studied the relationship between the binary interaction parameter, k_{ij}, with the temperature and with the molecular mass of some families of compounds. In Fig. A.7, the influence of the molecular mass of alkanes is studied in some acetic acid-alkanes systems, in which a second-degree behaviour is notorious. Moreover, as expected, Ali [60] also found that the co-volume presented a very similar relation with the molecular mass of hydrocarbons as well, as Fig. A.8 illustrates.

From Figs. A.6 and A.8 it can be concluded that the co-volume and the energy term parameter vary in a very linear fashion with the molecular mass, pretty similarly to what happens with the van der Waals volume in Schlaikjer's [8] results. Actually, after noticing that the average absolute deviations (AAD) in Schlaikjer's [8] work were still relatively high, Hansen [9] tried to fit trend equations to the experimental data, rather than the individual parameters, to primary alcohols, amines and carboxylic acids, increasing the quality of the predictions. In his method, named "trend fit method", firstly, second degree trends were supposed to all five parameters, secondly, they were fitted to experimental saturation pressure and liquid density data, minimising the objective function (OF) of equation 3.46.

$$\mathrm{OF} = \sum_{i=1}^{N_\mathrm{C}} \sum_{j=1}^{N_\mathrm{D}} \left(\frac{P^{\mathrm{sat}}_{\mathrm{CPA},i,j} - P^{\mathrm{sat}}_{\mathrm{exp},i,j}}{P^{\mathrm{sat}}_{\mathrm{exp},i,j}} \right)^2 + \left(\frac{\rho^{\mathrm{sat}}_{\mathrm{CPA},i,j} - \rho^{\mathrm{sat}}_{\mathrm{exp},i,j}}{\rho^{\mathrm{sat}}_{\mathrm{exp},i,j}} \right)^2 \tag{3.46}$$

Where N_C denotes the number of compounds, N_D is the number of data points, $P_{\mathrm{CPA},i,j}$ is the saturation pressure predicted by the CPA EoS model, $P^{\mathrm{sat}}_{\mathrm{exp},i,j}$ is the experimental saturation pressure, $\rho_{\mathrm{CPA},i,j}$ is the liquid density predicted by the CPA EoS model and $\rho^{\mathrm{sat}}_{\mathrm{exp},i,j}$ is the experimental liquid density.

This method of correlating equations relating the CPA EoS model parameters with the van der Waals volume directly to experimental data presented very good results for the chemical families tested, moving closer to a more predictive model. Regarding Fig. A.9, it can be noticed that the trend fit parameters have a generally better performance than the ones obtained from individually fitted parameters, the "classical" method, for the Vapour-liquid equilibrium (VLE) of heptane (1) and propanoic acid (2) at T = 348.15 K, i.e., the experimental values (✻) are closer to the line obtained from the trend fit method (—) than from the individual parameter fitting one (- -).

In the literature, some other studies focused on enhancing the predictiveness of the binary interaction parameter. For instance, Coutinho *et al.* [27] focused on understanding the influence of the number of carbons in the chemical structure and of the system asymmetries, for example, the ratio of van der Waals volumes between two species, in the binary interaction parameter, k_{ij}, and in the exponent n, a parameter required in the calculation of k_{ij}.

In Fig. A.10, it can be seen how the ratio of van der Waals volumes (with the biggest value as numerator) greatly influences the exponent n. Following, Fig. A.11 shows how the number of structural carbons can as well be a good tool to study the binary interaction parameter. Although, this relationship derives from its dependence with the van der Waals volume and doesn't provide that much information. Even though the two last referred figures represent the outcome of a study with the Peng-Robinson EoS, they can be a very good source of inspiration for this project's studies with the CPA EoS.

To sum up, several different authors worked already on finding relations between parameters and in increasing the predictiveness of this project's models. However, they are all based on (now) relatively old parameters and too focused on particular families. Hence, a more extensive database with a broader approach and further relations is required to enable the development of a more predictive CPA EoS model, since it is still impossible to correlate the vast majority of the needed parameters at the moment.

Chapter 4

Studies of dependence in pure compounds

In this chapter, it is intended to search for well-defined relations between the previously stated pure compounds' parameters with the aim of enhancing the predictiveness of the CPA EoS.

4.1 Database

In the Appendix C, a database can be found putting together the most relevant information for 197 different chemical compounds, namely, the energy term parameter, the corrected energy term parameter, the co-volume, the other energy term parameter (from Table C.1 to C.7), the molecular mass, the van der Waals surface area, the van der Waals volume (from Table C.10 to C.16), the association energy parameter, the association volume, the association scheme (from Table C.19 to C.20), the critical temperature and the critical pressure (from Table C.22 to C.27). The acquired data comprise compounds from 18 different chemical families, with especial preponderance of esters and alkanes, as Table 4.1 shows.

Table 4.1: Number of compounds in the database per chemical family.

Chemical Family	Number	Chemical Family	Number	Chemical Family	Number
Alcohols	16	Bromides	2	Ketones	6
Aldehydes	3	Carboxylic acids	2	Polyols	6
Alkanes	39	Chlorides	3	Sulfides	4
Alkenes	6	Cycloalkenes	3	Thiols	5
Amines	10	Esters	43	No well-defined family	7
Anhydrides	1	Ethers	8		
Aromatics	21	Fluorocarbons	12	**Total**	**197**

Although this division is somewhat subjective, i.e., some compounds may have different groups and only one must be chosen to attribute a chemical family, the quality of the classification can only be evaluated later, when the properties are plotted, since each group affects the parameters in different and unpredictable ways.

So as to construct the extensive database, firstly, all the data were collected from the literature, converted to useful units, organised and stored in Microsoft Excel, in a process which took several weeks. It must be said that part of the data from Table C.1 to C.7 and published before the year of 2012 was already grouped in a technical report by Tsvintzelis *et al.* [61]. All the different references which provided the data to create the database were properly referenced in the Appendix C.

Afterwards, all the missing parameters were calculated, specifically, the van der Waals volume and surface area were determined using the data from Appendix B and Bondi's method, as explained before in section 3.6.1. Moreover, the energy term parameter a_0 and the corrected energy term parameter, Γ, were inter-converted in one another whenever one of them couldn't be found, making usage of equation 3.25. Thirdly, all the parameters were plotted against each-other in SigmaPlot 11.0, a similar tool to Microsoft Excel but more directed to plot representation, and their dependence studied. Later on, the information was organised in plots and tables in OverLeaf, a LATEX writing interface. The fluorocarbons family was excluded from plot representation since it presented a completely different behaviour, as already reported by Kontogeorgis *et al.* [4] and Schlaikjer [8]. However, their plots will be analysed later.

As expected after reading the studies of Schlaikjer [8] and Palma *et al.* [59], a second-degree relation was found between the energy term parameter, a_0, and the van der Waals volume, V_w, as Fig. 4.1 illustrates.

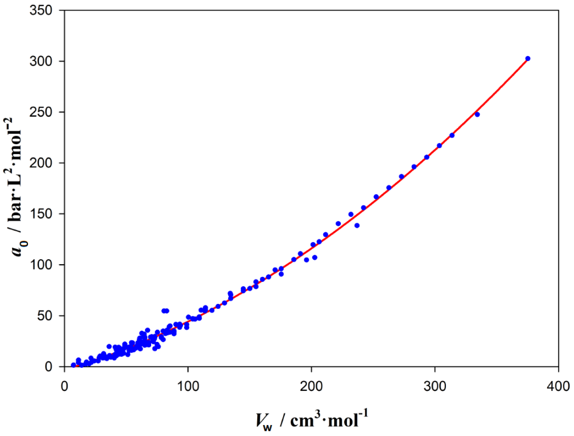

Fig. 4.1: Study of dependence of the energy term parameter, a_0, with the van der Waals volume, V_w. The regression (–) follows equation $a_0 = 1.25 \cdot 10^{-3} \cdot V_w^2 + 0.34 \cdot V_w - 2.84$, with a determination coefficient of 0.9941.

The compounds with smaller van der Waals volume (less than 100 cm^3·mol^{-1}) are far more abundant than the others and they include the species with the highest deviations from the fit. In the high-values zone of V_w, only long-chain alkanes are present, which seem to be well-predicted by the fit. Overall, the regression seems very good and apparently indicates that it is possible to accurately determine the energy term parameter only with the van der Waals volume. If fluorocarbons were considered, a few outliers would be found, decreasing the quality of the fit, as can be observed in Fig. D.2, in the Appendix D.

To what concerns the dependence of the co-volume parameter and the van der Waals volume, a second-degree relation was found, Fig. 4.2, with a determination coefficient of 0.9931. This is slightly different from the linear one reported by Schlaikjer [8], even though it can be said a first-degree regression could as well be performed, as Fig. D.1 shows, with a determination coefficient of 0.9928. Once more, the left side of the plot, i.e., smaller V_w, comprises the majority of the species and the right side is ruled by the behaviour of heavy alkanes.

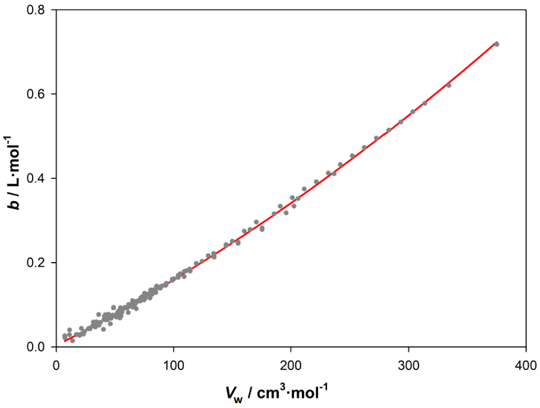

Fig. 4.2: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w. The regression (–) follows equation $b = 1.32 \cdot 10^{-6} \cdot V_w^2 + 1.42 \cdot 10^{-3} \cdot V_w + 3.64 \cdot 10^{-3}$, with a determination coefficient of 0.9973.

Lastly, having in consideration the similarity of their behaviours when plotted against the van der Waals volume, the energy term parameter, a_0, and the co-volume parameter, b, were represented together in Fig. 4.3, showing a unexpectedly good second-degree relation.

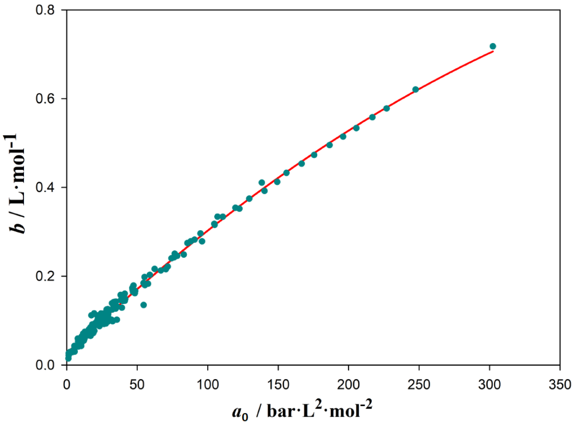

Fig. 4.3: Study of dependence of the co-volume parameter, b, with the energy term parameter, a_0. The regression (–) follows equation $b = -2.53 \cdot 10^{-6} \cdot a_0^2 + 3.01 \cdot 10^{-3} \cdot a_0 + 0.03$, with a determination coefficient of 0.9925.

When looking at Figs. 4.1, 4.2 and 4.3, a small step towards predictiveness must be noticed. The three studied parameters showed pretty good second-degree fits between each-other, apparently allowing to know all three parameters (a_0, V_w and b) with rather accuracy based on the knowledge of solely one.

So as to better understand the influence of the high molecular mass alkanes in the plots of Figs. 4.1, 4.2, 4.3 and D.1, four other representations were respectively done, Figs. D.9, D.10, D.12 and D.11, in which the species with molecular mass higher than 240 g·mol^{-1} were removed, corresponding to the alkanes which exceed to the right all the other chemical families. There, some reduction in the determination coefficients could be observed, specifically, from 0.9930 to 0.9758 in the energy term parameter, a_0, with the van der Waals volume, from 0.9931 to 0.9897 in the first-degree fit for the co-volume, b, with the van der Waals volume, from 0.9973 to 0.9918 in the second-degree one and from 0.9925 to 0.9789 in the co-volume parameter, b, with the energy term parameter, a_0. As expected, this part of the alkanes' family really influenced the regressions, improving all the results when taken into account. However. even without considering them, pretty good results can be obtained for the regressions, which would still allow to increment predictiveness.

Interestingly, the equations for the linear regressions in Figs. 4.1 and A.3, the latter performed by Schlaikjer [8], are pretty similar. In fact, all the pure compounds' data used in his work are present in this project database, so it is important to understand how different the databases are to take further conclusions. In Appendix D, a direct comparison is made between this project's pure compounds' database and the one earlier assembled by Schlaikjer [8] in his master's thesis. In total, 137 new chemical compounds were added in this project, with especial preponderance of esters (38), alkanes (24) and aromatics (20), as Table D.1 in Appendix D shows. When comparing the determination coefficients calculated from Schlaikjer's data and the ones obtained with the increased number of chemical species, a general lower value is found in the latter one, going from 0.9981 to 0.9928 and from 0.9994 to 0.9973 in the first and second-degree regressions of the co-volume, b, with the van der Waals volume, respectively, and from 0.9959 to 0.9941 in the energy term parameter, a_0, with the van der Waals volume. The plots and regression equations for the earlier database can be found in the appendices, in Figs, D.16, D.17 and D.18. Even though the determination coefficients became lower with the addition of new compounds, it is considered that they still represent very good fits, since a broader group of families is taken into account, strengthening the existence of a good relation between the parameters.

Additionally, the energy term parameter, a_0, and the co-volume, b, were also plotted against the molecular mass, but no good correlations could be found, as Figs. D.13 and D.14 show. Because of that, plotting them with the van der Waals volume seems to be the best option. On the other hand, good fits couldn't be found either for the energy term parameter c_1 with any of the other parameters, as Fig. D.15 shows, plotting c_1 with the van der Waals volume, V_w. Hence, this parameter must be fitted to experimental data.

Lastly, as forecast, Figs. D.2, D.3, D.4 and D.5, which include the fluorocarbons family, showed worse second-degree fits, with all four determination coefficients decreasing from 0.9941 to 0.9888, from 0.9973 to 0.9824, from 0.9928 to 0.9789 and from 0.9925 to 0.9780, respectively. Although this peculiar behaviour couldn't be explained, it is known that the Bondi's method is not supposed to be applied to fluorocarbons, so the calculated van der Waals volumes and surfaces areas can be different from the real values, maybe partially justifying this results. The chemical compound which deviated the most from the common behaviour traduced by the regressions was perfluorodecalin.

4.1.1 Alkanes

Alkanes are saturated hydrocarbons and their chemical structures evolve in a very predictable manner, with a linear growth in the van der Waals volume generally being verified, which is expected to permit some good relations between the parameters. As a consequence, a very good relationship was found between the van der Waals volume and the molecular mass, as it can be seen in Fig. D.19 in the Appendix D, with a determination coefficient of 1.0000. Following that, very good fits were also found for the co-volume parameter, b, with both the molecular mass, MM, and the van der Waals volume, V_w, as can be found in Figs. 4.4 and D.20, with determination coefficients of 0.9996. Moreover, the co-volume parameter, b, also showed pretty good relations with the energy term parameter, a_0, with the corrected energy term parameter, Γ, and with the critical temperature, T_c. All three can be observed in the appendices in Figs. D.22, D.23 and D.24, with determination coefficients of 0.9989, 0.9968 and 0.9978, respectively.

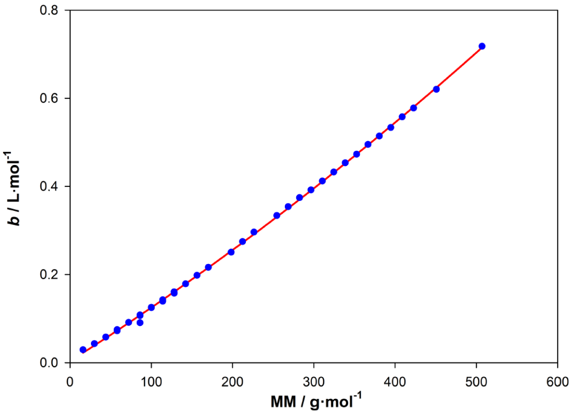

Fig. 4.4: Study of dependence of the co-volume parameter, b, with the molecular mass, MM, in alkanes. The regression (–) follows equation $b = 4.66 \cdot 10^{-7} \cdot \mathrm{MM}^2 + 1.17 \cdot 10^{-3} \cdot \mathrm{MM} + 3.47 \cdot 10^{-3}$, with a determination coefficient of 0.9996.

After some more studies, the critical temperature turned out to be even more important, with good relations found with both the energy term parameters, a_0 and c_1, which can be observed in Figs. D.25 and D.26 in the Appendix D, with determination coefficients of 0.9981 and 0.9954, by this order. Continuing the behaviour observed with all the compounds, the energy term parameter, a_0, showed a very good second-degree relation with the van der Waals volume. Besides that, having in mind the observed linear relation confirmed between the molecular mass and the van der Waals volume in alkanes, it also showed a very good second-degree relation with the molecular mass. Both fits can be seen in Figs. D.27 and 4.5, with determination coefficients of 0.9994.

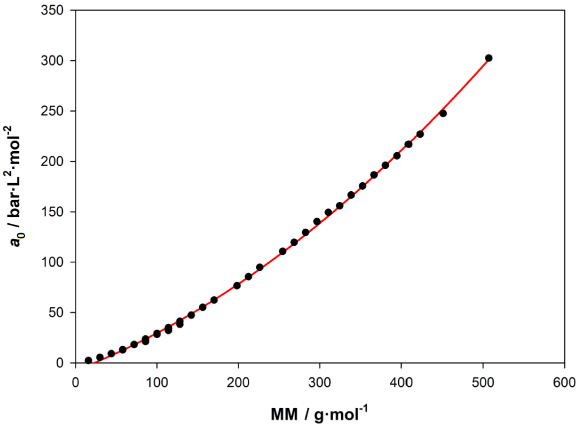

Fig. 4.5: Study of dependence of the energy term parameter, a_0, with the molecular mass, MM, in alkanes. The regression (–) follows equation $a_0 = 5.85 \cdot 10^{-4} \cdot \mathrm{MM}^2 + 0.31 \cdot \mathrm{MM} - 7.46$, with a determination coefficient of 0.9994.

Lastly, two more relations were found, this time between the corrected energy parameter, Γ, and both the molecular mass and the van der Waals volume, with determination coefficients of 0.9963. The respective plots are Figs. D.28 and 4.6. To do so, especial non-linear regressions were applied, following equation 4.1.

$$L_1 = k_1 \cdot (1 - e^{k_3 \cdot L_2}) + k_2 \cdot (1 - e^{k_4 \cdot L_2}) \tag{4.1}$$

Where k_1, k_2, k_3 and k_4 are the equation's adjustable parameters, L_1 is the dependent variable and L_2 is the independent variable. In these cases, the dependent variable is the corrected energy term parameter, Γ, and the van der Waals volume, V_w, or the molecular mass, MM, are the independent ones.

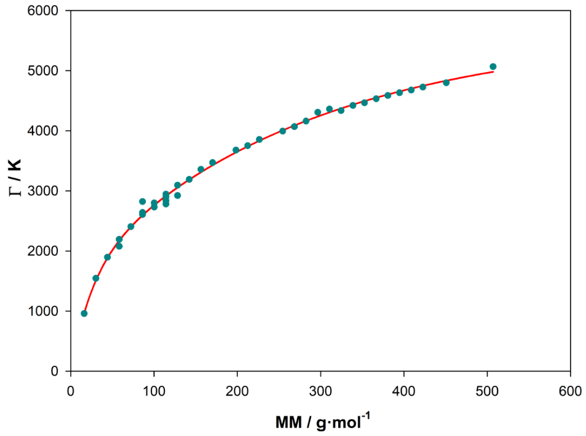

Fig. 4.6: Study of dependence of the corrected energy term parameter, Γ, with the molecular mass, MM, in alkanes. The regression (–) follows equation $\Gamma = 1.55 \cdot 10^3 \cdot (1 - e^{-0.0400 \cdot \mathrm{MM}}) + 4.08 \cdot 10^3 \cdot (1 - e^{-0.00363 \cdot \mathrm{MM}})$, with a determination coefficient of 0.9963.

In conclusion, some especial properties in alkanes, as the absence of polar segments, the non-existence of association, the similarities between all the compounds and their sequential construction from smaller to bigger molecular masses by the addition of methylene groups allow the parameters to be easily predicted by knowing only one.

4.1.2 Association energy and association volume

Initially, the association energy parameter, ε, didn't seem to have a particularly well-defined relation with any of the other parameters, showing a somewhat random distribution in all the chemical families studied, as it can be seen with the van der Waals volume, V_w, in alcohols, amines and polyols in Fig. D.32 in the appendices. Yet, a good non-linear relation was found for all the associating compounds except hydrogen sulfide and water (considered outliers) between a function of the energy term parameter and of the association energy parameter, $\varepsilon/(R_g \cdot a_0^2)$, and the van der Waals volume, V_w, as Fig. D.33 shows, for a regression type following equation 4.2 with a determination coefficient of 0.8556.

$$L_1 = k_1 \cdot e^{k_3 \cdot L_2} + k_2 \cdot e^{k_4 \cdot L_2} \tag{4.2}$$

Where k_1, k_2, k_3 and k_4 are the equation's adjustable parameters, L_1 is the dependent variable and L_2 is the independent variable. In this case, the dependent variable is a function of the association energy and of the energy term parameter, $\varepsilon/(R_g \cdot a_0^2)$, and the independent one is the van der Waals volume, V_w.

In spite of heavily relying on the relationship between the energy term parameter and the van der Waals volume, present in Fig. D.34 with a determination coefficient of 0.9947, the prediction of the association energy parameter seems to be ensured with relative accuracy if the other two parameters are known. Both correlations can be seen in more detail in Figs. D.35 and D.36, in which the chemical families are shown.

After a few more studies, it was noticed that the relation could be improved by the addition of a term having in consideration both the squared critical pressure and the critical temperature. Hence, the function $\varepsilon \cdot P_c^2/(R_g \cdot a_0^2 \cdot T_c)$ was plotted with the van der Waals volume, as Fig. D.37 shows, with a determination coefficient of 0.9998 for a regression type following equation 4.2. To better study the curve, other two alternative representations were performed: in the first one, the water was considered an outlier and a determination coefficient of 0.9180 was obtained, as Fig. D.38 shows; in the second one, a representation per family of the latter was undergone, present in Fig. D.39. On the other hand, no good relations could be found for the association volume, β. As a consequence, this parameter won't be predicted but fitted to experimental data.

4.1.3 Comparing the energy parameters

In Table D.2, different regressions performed for both the parameters can be observed and their determination coefficients compared. As can be seen there, the regressions for the energy term parameter a_0 with the van der Waals volume, V_w, with the co-volume, b, and with the molecular mass, MM, always present higher values for the determination coefficients than the ones for the corrected energy term parameter, Γ. Moreover, the latter usually needs more complex functions with a higher number of adjustment parameters, for example, as showed in equation 4.1. As a result, the energy term parameter a_0 seems more adequate to establish relations with and should be preferred to the corrected energy parameter, Γ.

4.1.4 Comparing the van der Waals properties

After having calculated the van der Waals surface areas, A_w, for the compounds present in the database with equations 3.38 and 3.40, the values were organised from Table C.10 to C.16 and some plots were represented. As forecast, this parameter presented a very good linear relation with the van der Waals volume, V_w, with a determination coefficient of 0.9934, as Fig. D.40 shows. Moreover, it also presented very good results for the fits with the energy term parameter, a_0, and with the co-volume, b, with determination coefficients of 0.9983 for the first case, 0.9883 for the second-degree fit with the co-volume and 0.9831 for the first-degree fit with the co-volume. These results can be observed in Figs. D.41, D.42 and D.43, respectively. When the fluorocarbons family was considered in the three last mentioned regressions, the determination coefficients decreased, as expected, being reduced from 0.9983 to 0.9777 and to 0.9756 in the first two cases and from 0.9831 to 0.9673 in the latter one. The pictures supporting these statements can be found from Fig. D.6 to D.8, by this order.

With the purpose of better comparing the van der Waals surface area, A_w, and the van der Waals volume, V_w, Table D.3 was created. It presents the most relevant fits, determination coefficients and regression types for both properties. There, it can be observed that all the studied regressions obtained with the van der Waals volume have higher determination coefficients than the ones which used the van der Waals surface area, with this difference being less important in alkanes but critical in associating compounds. Hence, the van der Waals volume is a better option than the van der Waals surface area to establish relations with, even though the usefulness of the second one should not be disregarded in cases in which there are no data for the van der Waals volume.

4.1.5 Critical properties

A good fit was found between the function $T_\mathrm{c}^2/P_\mathrm{c}$ and the energy term parameter, a_0, presenting a determination coefficient of 0.9819, as Fig. D.44 illustrates. Moreover, two good fits were also found between another function of the critical properties, $T_\mathrm{c}/P_\mathrm{c}$, and the co-volume, b, with a determination coefficient of 0.9768 in the first-degree regression and 0.9938 in the second-degree one, as Figs. D.45 and 4.7 respectively show.

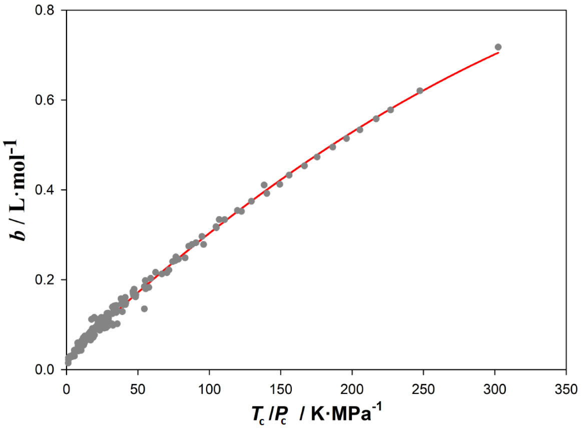

Fig. 4.7: Study of dependence of the co-volume, b, with a function of the critical properties, $T_\mathrm{c}/P_\mathrm{c}$. The regression (–) follows equation $b = -2.58 \cdot 10^{-6} \cdot (T_\mathrm{c}/P_\mathrm{c})^2 + 3.02 \cdot 10^{-3} \cdot T_\mathrm{c}/P_\mathrm{c} + 0.03$, with a determination coefficient of 0.9938.

Lastly, the van der Waals surface area also showed a pretty good relation with $T_\mathrm{c}/P_\mathrm{c}$, as Fig. D.46 presents, with a determination coefficient of 0.9837. This way, despite not presenting the highest determination coefficients, the critical properties can also become useful in the future, perhaps being possible to predict the parameters with these intrinsic properties and without needing previous knowledge on any other parameter.

Chapter 5

Predicting properties in pure compounds

In this chapter, vapour pressure and liquid density values predicted using the CPA EoS and following four different methods shall be compared with some correlations derived from experimental data. All the compounds in this project's database, with the exception of fluorocarbons, terephthalic acid and glycerol, will be considered. Besides, some other species couldn't be found in the experimental correlations' database, which were properly referred in Appendix E and decreased the total number of analysed chemical compounds to 174.

The first method of predicting vapour pressure and liquid density relied on the CPA EoS and used the parameters presented in Appendix C, in what can be described as the "classical" prediction fashion, since it only uses parameters from the literature. Next, the second method was also based on the CPA EoS, but it made usage of some correlated parameters, i.e., parameters predicted from other parameters or from chemical properties. Specifically, the co-volume, b, was calculated from the van der Waals volume, V_{w}, using the equation previously presented in Fig. 4.2, equation 5.1.

$$b = 1.32 \cdot 10^{-6} \cdot V_{\mathrm{w}}^2 + 1.42 \cdot 10^{-3} \cdot V_{\mathrm{w}} + 3.64 \cdot 10^{-3} \tag{5.1}$$

Moreover, in the second method, the corrected energy term parameter, Γ, was determined using both the already mentioned correlated co-volume and the energy parameter, a_0, which was obtained from the equation shown in Fig. 4.1, equation 5.2, and is also a function of the van der Waals volume. All the other parameters used are in Appendix C.

$$a_0 = 1.25 \cdot 10^{-3} \cdot V_{\mathrm{w}}^2 + 0.34 \cdot V_{\mathrm{w}} - 2.84 \tag{5.2}$$

On the other hand, the third method used the same correlated parameters as the second method and additionally fitted the energy term parameter c_1. This method should outperform the second one, since the fitting of one parameter is expected to minimise deviations. All the remaining parameters are present in Appendix C.

Lastly, the fourth method used the correlated version of the co-volume, b, and fitted both the corrected energy term parameter, Γ, and the energy term parameter c_1. Because of an increased number of fitted parameters, this method should more accurately describe liquid density and vapour pressure than the second and third ones. Following, Table 5.1 sums up how the values of the parameters were obtained. All the parameters missing were picked from the literature and their values can be seen in Appendix C, as previously mentioned.

Predicting properties in pure compounds

Table 5.1: Procedures taken for the CPA EoS parameters in the four different predictive methods for liquid density and vapour pressure.

Method	**Corrected energy term parameter (Γ)**	**Co-volume (b)**	**Energy term parameter (c_1)**	**Association energy (ε)**	**Association parameter (β)**
1	[a]	[a]	[a]	[a]	[a]
2	Correlated	Correlated	[a]	[a]	[a]
3	Correlated	Correlated	Fitted	[a]	[a]
4	Fitted	Correlated	Fitted	[a]	[a]

[a] Literature values presented in Appendix C.

Furthermore, some correlations from the Design Institute for Physical Properties (DIPPR) and deeply based in experimental data were used. They were found in the DIADEM Professional program, which was used under CERE's licence, and allowed a quick analysis of the performance of the four methods without the need of gathering a huge amount of experimental data. Given their big accuracy, the results obtained from the other methods should be the closest possible to these ones to ensure a good prediction in real applications.

In all the methods, a temperature range from $0.5 \cdot T_c$ to $0.95 \cdot T_c$ with a step of 1 K were considered. However, some big differences were noticed between the critical temperatures from the DIADEM Professional database and the ones obtained from the literature and some readjustments had to be done in the calculations not to surpass the smallest of those two critical temperatures, which would be outside of the domain of the model. A comparison of these temperatures can be observed in Fig. 5.1, where it can be seen that some values are very different. In particular, the critical temperatures of cyanogen chloride, indole and methyl tetradecanoate had to be changed to correspond the ones in the DIADEM Professional database because of extremely big AAD's.

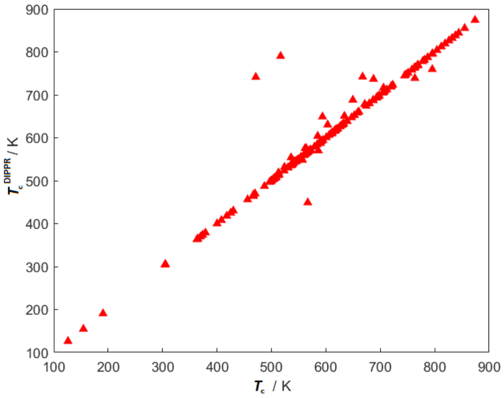

Fig. 5.1: Comparison between the critical temperature values stored in this project's database, T_C, and the ones from the DIADEM Professional database, $T_\mathrm{C}^\mathrm{DIPPR}$.

Considering the substantial number and complexity of the calculations, a Visual Basic for Applications (VBA) macro was created to reorganise and export the data from Microsoft Excel to MATLAB. Particularly to what concerns CPA EoS-related calculations, an especial group of MATLAB functions developed in CERE [62, 63] was applied to the analysis of the database, easing calculations to a great extent. The code was meant to make usage of these functions in an efficient way, to save all the outputs, to perform all the additional calculations and to plot the most important results. For all the methods, the bubble point, i.e., saturated vapour pressure, and the compressibility factor, Z, were obtained straight away from CERE's functions [62,63]. Afterwards, the liquid densities were calculated following equation 5.3.

$$\rho_{\mathrm{L}} = \frac{P_{\mathrm{sat}} \cdot \mathrm{MM}}{Z \cdot R_{\mathrm{g}} \cdot T} \tag{5.3}$$

Where ρ_{L} is the liquid density, P_{sat} is the saturation pressure, MM is the molecular mass, Z is the compressibility factor, R_{g} is the ideal gas constant and T is the temperature; all them are in SI units. Since the saturated vapour pressure is assumed, these were considered saturated liquid densities.

In the third and fourth methods, some extra calculations were needed, since the referred parameters were iterated using the objective function present in equation 3.46. Later, for all the methods, the average absolute deviation (AAD), i.e., an arithmetic mean of all the absolute deviations, was calculated following equation 5.4 and considering the DIPPR correlations as reference.

$$\mathrm{AAD} = \sum_{i=1}^{\mathrm{NC}} (\mathrm{AD})/t \tag{5.4}$$

Where AAD is the average absolute deviation, AD stands for absolute deviation, calculated by equation 5.5, and t stands for the total number of elements analysed.

$$\mathrm{AD} = \left| \frac{Y_{\mathrm{method}} - Y_{\mathrm{DIPPR}}}{Y_{\mathrm{DIPPR}}} \right| \cdot 100\ \% \tag{5.5}$$

Where Y_{method} is a generic property calculated by one of the methods and Y_{DIPPR} is the value of that property when following the DIPPR correlations.

The results of the predictions of properties are summarised in table 5.2 for all the methods.

Table 5.2: Average absolute deviations (AAD) and number of analysed temperatures for the predictions of vapour pressure and liquid density in all four methods.

	Vapour pressure	**Liquid density**	
Method	**AAD / %**	**AAD / %**	**Convergences**
1	3.7	2.0	46 640
2	59.4	6.0	46 188
3	14.1	4.7	46 430
4	1.5	3.7	46 640

After comparing the first and second methods, it seemed clear that the results could be strongly affected by replacing a_0 and b by their correlated versions, with the calculations of vapour pressures being significantly more sensitive. As foreseen, the fitting of c_1 and Γ significantly diminished the deviations and increased the convergence of the calculations for both the properties. Another curious fact is how almost unaffected the calculations of liquid density seem to be by high AAD in the vapour pressures, which can be noticed from the passage of the first to second methods.

In Appendix E, some figures allow the reader to establish a comparison between the energy term parameter, the co-volume and the corrected energy term parameter and their values obtained from the correlations. There, the first two parameters present high determination coefficients for a first-degree regression, i.e. their values and their correlated ones are almost the same, specifically, with 0.9943 and 0.9977, as can be seen in Figs. 5.2 and 5.3, respectively.

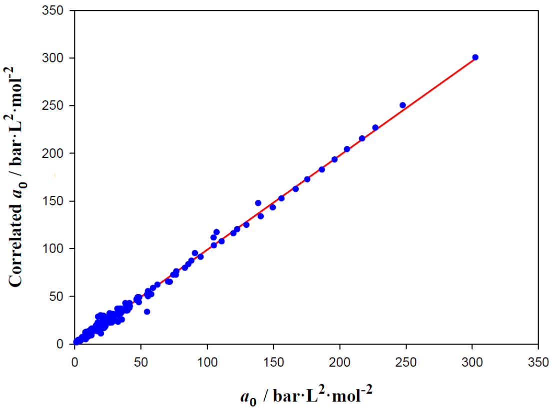

Fig. 5.2: Comparison between the energy term parameter values stored in this project's database, a_0, and the correlated ones, $a_0^{\text{corr.}}$. The regression (–) follows equation $a_0^{\text{corr.}} = 0.99 \cdot a_0 + 0.14$, with a determination coefficient of 0.9943.

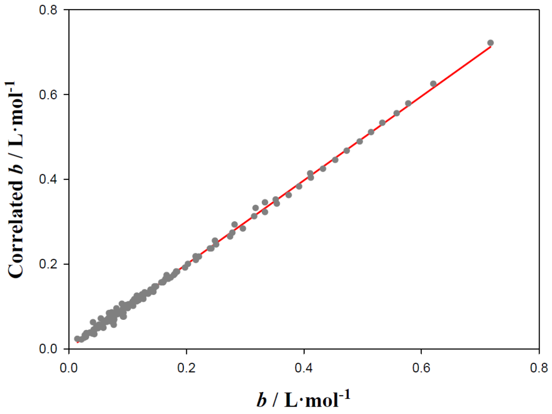

Fig. 5.3: Comparison between the co-volume values stored in this project's database, b, and the correlated ones, $b^{\text{corr.}}$. The regression (–) follows equation $b^{\text{corr.}} = 0.99 \cdot b$, with a determination coefficient of 0.9977.

Although, when it came to the corrected energy term parameter the determination coefficient drastically fell to 0.7887, which means that the correlated Γ is, in general, very different than the theoretical value, as can be seen in Fig. 5.4. This way, it seemed obvious that the prediction of the corrected energy parameter is heavily affected by small deviations of the co-volume and of the energy term parameter, a_0. Being so, the deviations in the determination of Γ explain some of the deviations found in the second and third methods. Moreover, as mentioned before, the prediction of vapour pressures is substantially more affected than the prediction of the liquid densities.

Predicting properties in pure compounds

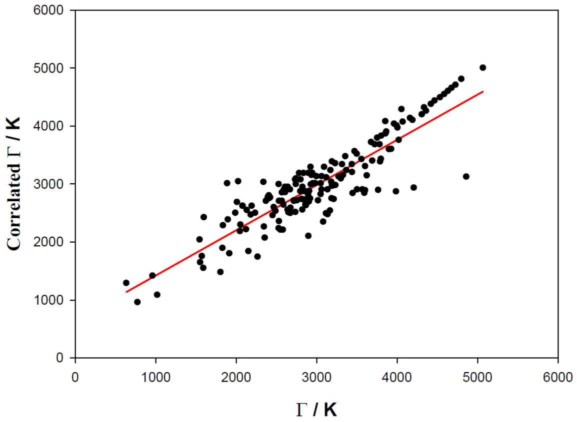

Fig. 5.4: Comparison between the corrected energy term parameter values stored in this project's database, Γ, and the correlated ones, $\Gamma^{\text{corr.}}$. The regression (–) follows equation $\Gamma^{\text{corr.}} = 0.80 \cdot \Gamma + 642.53$, with a determination coefficient of 0.7887.

Afterwards, the distribution of the average absolute deviations was studied. Figs. 5.5 and E.9 show the representation of AAD with the molecular mass for methods 3 and 4 for the calculations of vapour pressure and liquid density, respectively. There, a general decrease of the value of deviations can be observed for the vapour pressure in the method 3 with the molecular mass, which is a good result since the majority of the species with unknown parameters, so in which a more predictive model is needed, are heavy compounds.

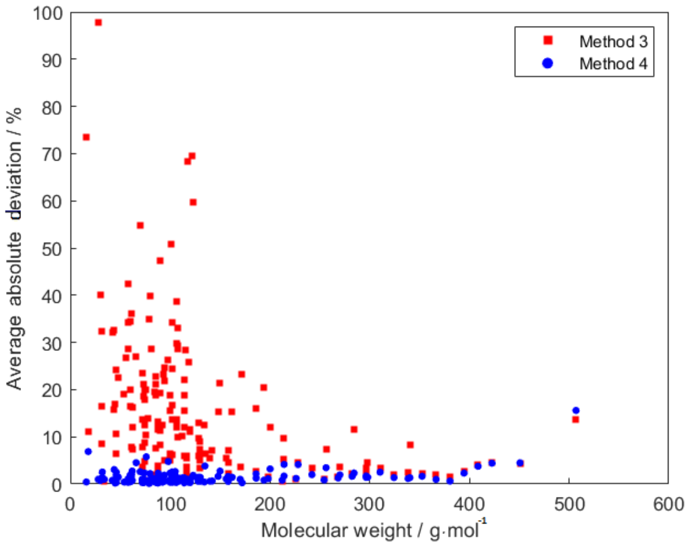

Fig. 5.5: Average absolute deviations (AAD) in the calculation of vapour pressure following methods 3 and 4 with the molecular mass.

In Fig. E.9, it can also be seen that the deviations in the liquid density almost haven't changed from method 3 to method 4 even though Γ was fitted, showing once more that the calculations of vapour pressure are significantly more sensitive to variations in Γ than the ones of liquid density.

Additionally, in the appendices, eight other figures represent the best cases, i.e., smallest AAD, for all the methods. The vapour pressures obtained from the different methods can be observed for the compound with the smallest error in each of the four methods, by ascending order, in Figs. E.1, with an AAD of 0.1 % for tetrahydrothiophene, Fig. E.2, with an AAD of 0.9 % for isobutanol, Fig. E.3, with an AAD of 0.6 % for hydrogen sulfide, and Fig. E.4, with an AAD of 0.1 % for pyridine.

Following, they can be seen for the liquid densities, by ascending order in the number of the method, in Fig. E.5, with an AAD of 0.2 % for acetic acid, Fig. E.6, with an AAD of 0.7 % for 1-hexanol, Fig. E.7, with an AAD of 0.7 % for 1-pentanol, and Fig. E.8 with an AAD of 0.6 % for methyl ethanoate. Obviously, these eight figures only speak for themselves and too general conclusions can't be taken involving all compounds straight away, but it is now clear that it is possible to predict some CPA EoS parameters based on other parameters or in chemical properties as well as based on fitted parameters and still have relatively good results.

All the new parameters, i.e., the correlated and fitted versions of Γ and c_1, can be seen from Table E.1 to E.7 in the appendices. To better analyse the data, AAD were calculated for each chemical compound, from Table E.8 to Table E.23, and for each chemical family in Tables E.24 and E.25. From there, it is obvious that the AAD are always smaller in the first method, when compared to the second and third methods, which was expected since the CPA EoS parameters are fitted to liquid density and saturation pressure data in order to be obtained.

Although the second method presented some good results, especially in esters and when predicting liquid densities, a significant part of the calculations in this method was really sensitive to the deviations in the value of the correlated corrected energy term parameter, $\Gamma^{\text{corr.}}$, and several unacceptable results were obtained, with some AAD way higher than 100 %, generally in the vapour pressures, and which simply cannot be used. In spite of a fraction of these deviations might also be explained by the sometimes slightly different van der Waals volumes used by the DIPPR correlations in the calculations, them alone couldn't explain the results. Therefore, the cause can rely in the temperature range in which the CPA EoS parameters were calculated in the literature, often smaller than the interval $0.5 \cdot T_C$ to $0.95 \cdot T_C$ used in this project. In addition, and even though the parameters were checked several times, some of them could have been wrongly read in the literature or their value could not have been determined properly. Even though the third method hasn't completely solved the big deviations found in the second one, it really improved its predictive capability, enhancing results' quality every time it was applied.

Moreover, when comparing the first and fourth methods, it can be seen that sometimes the latter has a better performance than the former, which is really good, but is probably due to the usage of different properties in the cited works and different temperature ranges. The most important thing to retain of this is that the fourth method can match the predictions of the pure CPA EoS even though it uses one correlated and two fitted parameters. If regarded carefully, it can be seen how outstanding this result is, especially in non-associating compounds, since no parameters were used from the literature and all them were predicted from chemical properties or fitted to experimental data.

Finally, from all this, it can be seen that it is possible to predict and fit some CPA EoS parameters and to successfully apply them, obtaining good results under some circumstances and avoiding the need of parameters from the literature, especially in the fourth method, in what is a big push towards an increased predictability.

Chapter 6

Studies of dependence in binary mixtures

In this chapter, following the same path taken for pure compounds, some studies of dependence will be performed in binary mixtures. Specifically, studies concerning the binary interaction parameter k_{ij} and its respective exponent, n, from the Hudson-McCoubrey (HM) theory [47].

Firstly, a database was created for the binary interaction parameters and ionisation potentials [64], which can both be seen in appendix F. Then, a MATLAB code was written to calculate the cross-co-volumes by the arithmetic mean (AM) of the co-volumes and all the exponents n from the literature values of k_{ij} using both the "classical" HM theory, given by equation 3.32, and an approximate version, given by equation 3.35, which avoids the drawback of having to know the ionisation potentials for all species present.

The results can be observed from Table F.22 to F.30 for the first method and from Table F.31 to F.39 for the second one, both in appendix F, in which all data are sorted by growing entry number of the chemical compounds in this project's database, as early shown in appendix C. Further, the MATLAB code can be read in appendix G. Some of the ionisation potentials were not found in the literature, so the number of analysed pairs in the second method is bigger than in the first one, 219 and 171, respectively. Moreover, it must be taken into consideration that the temperature dependence of the binary interaction parameters was ignored and that an average value was considered.

After having plotted the ionisation potential with the van der Waals volume, Fig. F.1, and with the co-volume, Fig. F.2, no notorious tendencies were identified, so some further analysis were undergone per family. A very good non-linear relation was found in alkanes for both the van der Waals volume, Fig. 6.1, and co-volume, Fig. F.5, with determination coefficients of 0.9958 and 0.9905, respectively. Later, some other successful per family analysis were done, namely, in alcohols, Figs. F.3 and F.4, and in ethers, Figs. F.6 and F.7. As it can be seen by the figures in Appendix F, the correlations with the van der Waals volume and with the co-volume exhibit a very similar performance, with, especially in alkanes, the former being better than the latter.

Regarding previous efforts on this matter, Haslam *et al.* [65] showed a decreasing tendency of the ionisation potential with the carbon number in n-alkanes and Coutinho *et al.* [27] showed an increasing tendency of the ionisation potential with the inverse of the cubic molecular diameter, σ, in some hydrocarbons and in some gases. As it is known, the co-volume is approximately given by the cubic molecular diameter, also known as collision diameter, so this project's results agree with the previous studies, since a decreasing tendency was found between the ionisation potential and the co-volume for alcohols, alkanes and ethers. However, the relationship observed was an exponencial decay and not an approximate straight line as Coutinho *et al.* [27] described, probably because their analysis was performed on a smaller number of components.

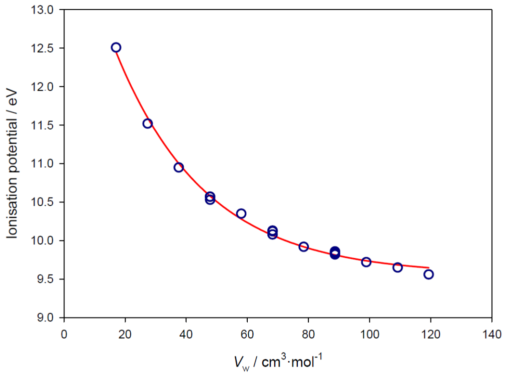

Fig. 6.1: Study of dependence of the ionisation potential, I, with the van der Waals volume, V_w, in alkanes. The regression (–) follows equation $I = 9.57 + 5.14 \cdot e^{-3.38 \cdot 10^{-2} \cdot V_w}$, with a determination coefficient of 0.9958.

Another important task was to study how the exponent n and the binary interaction parameter, k_{ij}, were related in both the methods with measures of system asymmetries, specifically, ratios of size parameters, as, for example, the ratio of van der Waals volumes and the ratio of co-volumes. During the calculations of these ratios, one can define the denominator as the biggest value or as the smallest one. In this project, the names "smaller ratio" and "bigger ratio" were accordingly given. After analysing all possible combinations between chemical families, it was notorious that, as expected, both the "bigger" and "smaller" ratios presented equivalent correlations with n and k_{ij}. However, the "bigger ratio", i.e., smaller denominator, was kept since it allows a faster understanding of how many times one molecule is bigger than the other.

For the combination alcohols-alkanes, no useful correlations were found directly including the binary interaction parameter. Although, two good correlations were found between the exponent n and both the bigger ratio of van der Waals volumes, V_{ratio}, Figs. F.8 and F.10, and the bigger co-volumes ratio, Figs. F.12 and Fig. F.14, for both methods, respectively. In order to ease the visualisation of the plots, four alternative representations were made in which the extremely high values of n were removed ($n > 20$), Figs. F.9, F.11, F.13 and F.15, respectively. As previously mentioned, the plots for the second method always have the same or higher number of points, since they don't require the knowledge of the species' ionisation potentials. For alkanes-polyols, the same correlations were studied for the calculated exponent n, although not so good, namely, with the ratio of van der Waals volumes in the first and second methods, Figs. F.16 and F.18, respectively, and with the ratio of co-volumes, Fig. F.20 and F.22. Following the same logic, four alternative representations were made in which the extremely high values of n were removed ($n > 20$), Figs. F.17, F.19, F.21 and F.23, respectively. For alkanes-water, good correlations were found for the calculated exponent n with the van der Waals volumes ratio, Figs. F.24 and F.25, and with the co-volumes ratio, Figs. F.26 and F.27, for the first and second methods, respectively. Moreover, additional good correlations were found for the binary interaction parameter, k_{ij}, with the van der Waals volumes ratio, Fig. 6.2, and with the co-volumes ratio, Fig. F.28.

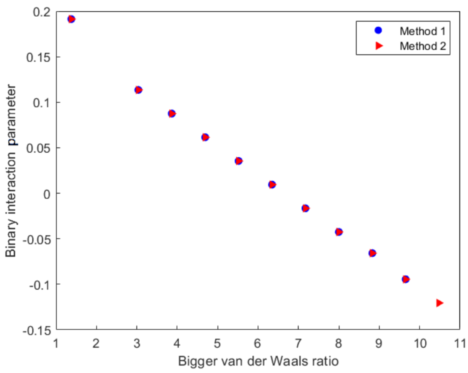

Fig. 6.2: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of van der Waals volumes in alkanes-water for both the methods.

For acetic acid-alkanes, some good correlations were found for the calculated exponent n with the van der Waals volumes ratio, Figs. F.29 and 6.3, and with the co-volumes ratio, Figs. F.30 and F.31, for the first and second methods, respectively.

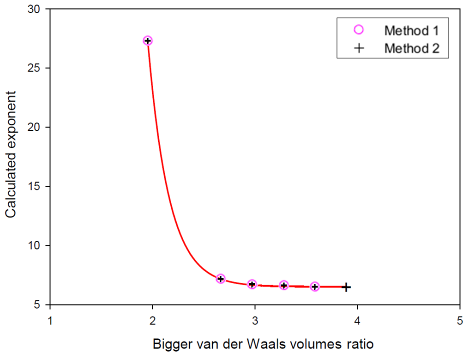

Fig. 6.3: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in acetic acid-alkanes for the second method. The regression (–) follows equation $n = 6.51 + 2.77 \cdot 10^5 \cdot e^{-4.86 \cdot V_{\text{ratio}}}$, with a determination coefficient of 1.0000.

On the other hand, extra correlations were found for the binary interaction parameter, k_{ij}, with the van der Waals volumes ratio, Fig. F.32, and with the co-volumes ratio, Fig. F.33. For BTEX (benzene, toluene, ethylbenzene and xylene)-water, the exponents for both methods can be seen with the bigger ratio of van der Waals volumes and co-volumes in Figs. F.34 and F.35, respectively. Moreover, for the binary interaction parameters the respective plots are Figs. F.36 and F.37 for both methods. For acetone-hydrocarbons, the exponents for both methods can be observed with the bigger ratio of van der Waals volumes and co-volumes in Figs. F.38 and F.39, by this order. To what concerns the binary interaction parameters, the respective plots are Figs. F.40 and F.41 for both methods. Following, for the combination alkanes-ethanol, the exponents for both methods can be seen with the bigger ratio of van der Waals volumes and co-volumes in Figs. F.42 and F.43, respectively. No good correlations were found for the binary interaction parameters. Further, for the combination alkanes-glycols, the exponents for both methods can be seen with the bigger ratio of van der Waals volumes and co-volumes in Figs. F.44 and F.45, respectively. No good correlations were found for the binary interaction parameters. Finally, only a relation between the exponents and the bigger ratio of co-volumes was found for alkanes-MEG, as Fig. F.46 shows. The following table, Table 6.1, summarises the majority of the results for the second method, which is the most practical and the one with the biggest number of points.

Table 6.1: Summary of the relations found for the exponents n and for the binary interaction parameter (k_{ij}) with the bigger van der Waals volumes ratio (V_{ratio}) and with the bigger co-volumes ratio (b_{ratio}) in the second method for different chemical pairs.

	Exponent n		k_{ij}	
Chemical pairs	V_{ratio}	b_{ratio}	V_{ratio}	b_{ratio}
Acetic acid-Alkanes	✓	✓	×	×
Acetone-Hydrocarbons	✓	✓	✓	✓
Alkanes-Ethanol	✓	✓	×	×
Alkanes-Ethers	×	×	×	×
Alkanes-Glycols	✓	✓	×	×
Alkanes-MEG	×	✓	×	×
Alkanes-Polyols	✓	✓	×	×
Alkanes-Water	✓	✓	✓	✓
Aromatics-Water	×	×	×	×
BTEX-Benzene	✓	✓	✓	✓
Ethers-Water	×	×	×	×

✓ - Good relation found.

× - No good relation found.

Having finished all the analysis, it seems easier to find good correlations for the exponent n than to the binary interaction parameter. In fact, reasonable values for the exponents (between 0 and 10) were obtained using both the methods applied. Though, when the species in the chemical pair under study were too similar, i.e., small asymmetries, the denominator in equation 3.35 became almost zero and the exponents assumed really high absolute values, as Figs. F.47 and 6.4 show for the second method.

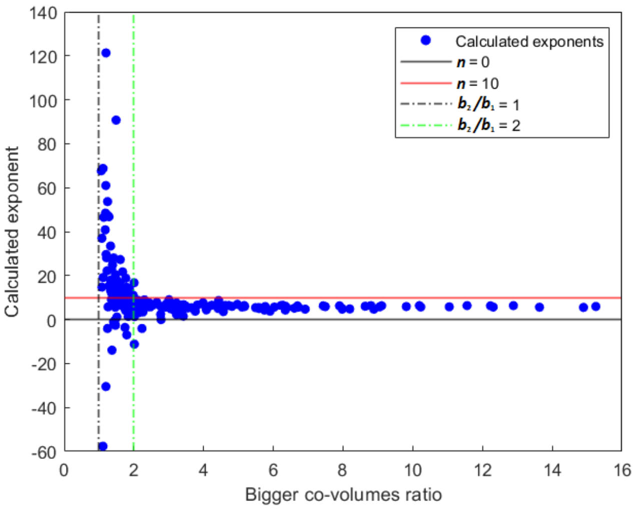

Fig. 6.4: Study of dependence of the calculated exponents n with the bigger co-volumes ratio for all the combinations with the second method.

In these figures, it can also be noticed that, if the ratio surpasses the value of two, n becomes reasonable and, if the ratio becomes higher, an almost constant value is achieved. This is particularly interesting since this theory would be applied in combinations of compounds with high asymmetry and unknown properties. In spite of not having studied the same systems as Coutinho *et al.* [27] nor having used the same equation of state, some similar general remarks can be made, especially, a decrease of the exponent n with the growth of the bigger ratio of co-volumes. Since the co-volume is closely related to the van der Waals volume, the same behaviour was observed between the exponent n and the bigger van der Waals volumes ratio.

When comparing the first and second methods, the overall behaviour is really similar, although the exponents are slightly higher in the latter, as can be seen in Figs. F.48, F.49, F.50, F.51, F.52 and F.53. Even though the second method is more straightforwardly applied, the first one should be preferred whenever possible, since it is a more accurate expression. To what concerns the usage of the van der Waals volumes ratio compared to the ratio of co-volumes, it depends on the families under evaluation and they are normally very similar. However, in general, the ratio of co-volumes provides better results, as can be seen from comparing Figs. F.44 and F.45.

Regarding the binary interaction parameters, it must be said that they presented exactly the same values for both the methods because they were fitted to literature data, as can be seen in Figs. F.54, F.55, F.56 and F.57. Obviously, the exponents had to be different to account for the mathematical and theoretical differences between method 1 and method 2. When comparing results with Ali's [60] previous efforts, some common conclusions can be made, for example, that the binary interaction parameter decreased with an increase of the molecular mass of alkanes in the systems acetic acid-alkanes, as previously seen in Fig. A.7. In this project, the same was observed for an increasing bigger van der Waals volumes ratio, meaning that the binary interaction parameter decreases with system asymmetries. Even though they are not completely linearly related, a bigger ratio implies a molecule with bigger volume, so, generally, a bigger molecular mass.

Following, with the aim of analysing the sensitivity of the model, using the correlations from Figs. F.27 and F.31, the k_{ij} were predicted for alkanes-water and acetic-acid alkanes, as Figs. F.58 and 6.5 respectively show. In the first case, the model failed in predicting the linear relationship between k_{ij} and the ratio of the co-volumes. However, in acetic acid-alkanes a very good prediction was achieved, as it may be seen below. One must remember that the "theoretical values" were considered to be the ones from this project's database.

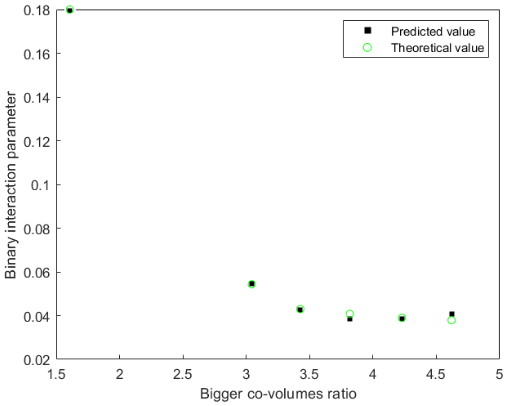

Fig. 6.5: Predicted binary interaction parameters, k_{ij}, in acetic acid-alkanes for the second method using the correlation $n = 6.45 + 9.40 \cdot 10^2 \cdot e^{-2.37 \cdot b_{\text{ratio}}}$, with a determination coefficient of 0.9948.

On the other hand, so as to study the sensitivity in a more general perspective, different positive and negative variations in the exponents n and their respective influences on the values of the binary interaction parameters k_{ij} were analysed in Figs. 6.6 and F.59, making a comparison with their "theoretical values", i.e., the values from the literature organised in appendix F.

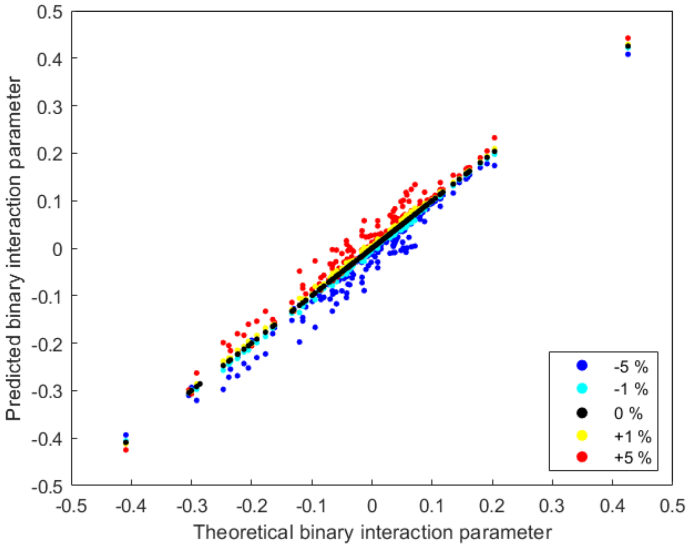

Fig. 6.6: Sensitivity analysis for small variations of the exponents n in the determination of the binary interaction parameters, k_{ij}, using the second method.

As it can be seen from the two previously referred figures, the model is really sensitive to small variations in the values of the exponents.

Finally, it can be said that the Hudson-McCoubrey theory was successfully applied and that some correlations found may be very useful in the prediction of the binary interaction parameters and of the exponents n. Moreover, the second method, i.e., the approximate expression not considering the ionisation potentials, ended up being a very good alternative whenever needed, correctly describing the species behaviours. Nevertheless, the model is relatively sensitive to variations in the exponents n and this fact may hamper the usage of correlations in some chemical families.

Chapter 7

Conclusions

The main goal of this project was to enlarge the predictability of the Cubic Plus Association (CPA) equation of state, a model which puts together the Soave-Redlich-Kwong (SRK) equation of state with the association term of the Wertheim theory. Other side objectives were to analyse the chance of application and the usefulness of group contribution theories and of the Hudson-McCoubrey theory in the prediction of parameters and properties to further decrease the need of experimental data and laboratory procedures. The CPA EoS requires a considerable amount of parameters to accurately describe the behaviour of chemical compounds. Specifically, three parameters are required for non-associating compounds, i.e., which don't establish hydrogen bounds, (co-volume, b, and the energy parameters c_1 and a_0) and five for associating compounds (a_0, b, c_1, the association energy, ε, and the volume of association, β). However, their values can only be estimated from experimental data, normally from vapour pressure and liquid density data, which implies a big necessity of acquiring large amounts of data and expensive experimental procedures, often hard to perform in the majority of the companies. Besides, only a small amount of the CPA EoS parameters is known and, with the lack of experimental data, especially to what concerns electrolytes, ionic liquids, pharmaceuticals, polymers and other heavy compounds, there is a significant need of finding ways of predicting them.

After having created a comprehensive database with CPA EoS parameters and properties for 197 chemical compounds, correlations between parameters and properties and between parameters and other parameters were searched for in all compounds and between groups of similar species. For example, very good second-degree correlations were found for all the compounds except fluorocarbons for a_0 with the van der Waals volume (R^2 = 0.9941), for b with the van der Waals volume (R^2 = 0.9973) and for b with a_0 (R^2 = 0.9925). The linear correlation of b with the van der Waals volume also had a high determination coefficient (R^2 = 0.9928).

In alkanes, probably because of their linear growth in van der Waals volume (V_w) with increasing chain length, apolarity and absence of association, several additional correlations were found. For instance, second-degree correlations between b and the molecular mass (MM) (R^2 = 0.9996) and non-linear correlations between b and both the corrected energy parameter Γ (R^2 = 0.9968) and critical temperature (R^2 = 0.9978). However, no reasonable correlations were discovered involving the fluorocarbons family and no explanation could be found for this fact.

Whenever absent in the literature, the values for the van der Waals volumes and areas (A_w) were determined following Bondi's method, a group contribution methodology. In general, the former showed better correlations than the latter. On the other hand, when comparing a_0 with the corrected energy term parameter, Γ, the correlations in which the first was present also showed higher determination coefficients with simpler mathematical functions.

Following, using the correlations found for pure compounds, four different methods were used in predicting vapour pressure and liquid density. The first used only CPA EoS parameters from the literature, the second used correlated values of both Γ and b, the third used the same correlated parameters and fitted c_1 and the last one correlated b and fitted both Γ and c_1. The predicted densities and pressures were compared to DIPPR data and, in all the methods, a temperature range from $0.5{\cdot}T_c$ to $0.95{\cdot}T_c$ with a step of 1 K was considered. In a total of about 46 000 convergences, liquid densities with AAD of 3.7 %, 54.9 %, 14.1 % and 1.5 % and vapour pressures with AAD of 2.0 %, 6.0, % 4.7 % and 3.7 % were obtained using the four methods, by ascending order. Hence, it seemed clear that in the prediction of the vapour pressure the results could be strongly affected by replacing a_0 and b by their correlated versions. Surprisingly, the fourth method even achieved a better result than the classical CPA EoS in calculating liquid densities, which can be explained by the usage of different parameters and properties than the ones present in DIADEM Professional by previous works. Overall, these results are promising since it is possible to predict and fit parameters using only simple properties and still have relatively good results. However, some of the calculations in this method were really sensitive to the deviations in the value of Γ and several AAD higher than 100 % were obtained, generally in calculating vapour pressures, which simply cannot be used. Therefore, the cause can rely in the temperature range in which the parameters were calculated in the literature, often smaller than the interval used in this project.

Then, some studies of dependence were undergone in binary mixtures. After a new database was completed, the exponents n for 219 binary interaction parameters (k_{ij}) were calculated using the Hudson-McCoubrey theory and following two different methods. In the first one, the "classical" theory was applied and in the second an approximate expression was used, not considering ionisation potentials. In general, very reasonable values were obtained for the exponents (between 0 and 10). Though, when the species in the chemical pair under study were too similar, i.e., small asymmetries, the denominator in the model's equation became zero and the exponents assumed really high absolute values. On the other hand, if the ratio surpassed the value of two, n became reasonable and, if the ratio became higher, an almost constant value was achieved. This is particularly interesting since this theory would be applied in compounds with high asymmetry and unknown properties. It must also be said that the second method ended up being a very good alternative whenever needed, correctly describing the species' behaviours even though it had a simplified mathematical expression. Later. the relationship between the calculated exponents and the measures of asymmetry, as the ratio of co-volumes and of van der Waals volumes, were studied. In this step, only the bigger ratios, i.e., the numerator is bigger than the denominator, were considered. Very good relations were found between the exponents n and the measures of asymmetry between alkanes and alcohols, glycols, polyols, acetic acid, ethanol, MEG and water and between BTEX-water and acetone-hydrocarbons. Although not so common, some correlations were also found for k_{ij} with the measures of asymmetry. Nevertheless, the model was considered to be sensitive to variations in the exponents n and that this fact could hamper the future usage of correlations in some chemical families.

In conclusion, by exploring the common behaviour of the properties of similar compounds, the predictability of the CPA EoS model was successfully enlarged while still presenting a good performance.

Chapter 8

Project assessment

In this final chapter, a self-critique will be performed to this project and some suggestions will be given for future work.

8.1 Degree of completion

Five different main objectives were aimed at in the start of this project. Firstly, reducing the number of needed CPA EoS parameters, secondly, decreasing the need of data tables and experimental procedures, thirdly, applying group contribution methods, fourthly, applying the Hudson-McCoubrey theory and, lastly, increasing the predictability of the Cubic Plus Association EoS model.

As can be stated from all the good correlations found and from the four methods applied in the prediction of vapour pressure and liquid density, it was shown that the number of needed CPA EoS parameters from the literature could be reduced, consequently diminishing the need of data tables and laboratory experiments. Hence, the first and second bullets were fully accomplished.

Regarding the group contribution methods, the Bondi's method was successfully applied in the determination of the van der Waals surface area and volume, fulfilling this secondary goal.

Concerning the Hudson-McCoubrey theory, the second suggestion from Schlaikjer [8] and Hansen [9] apart from the group contribution method, it was successfully applied in the determination of the exponents of the binary interaction parameters. Being so, this secondary objective was fully accomplished, even though it could have been more delved into if time was not a limiting condition, as it will be mentioned in the future work section.

From everything previously said, it is believed that some relevant steps were taken in the direction of a more predictive CPA EoS, heavily supported in common behaviour between alike chemical compounds, and ultimately achieving the prime objective of this project.

8.2 Additional work

No additional work was done besides everything directly related to this report and/or mentioned in the document. Although, during the five months of writing, a big amount of supplementary material, as code sections, plots and figures, unsuccessful correlations and hypothesis were created and couldn't be shown in the document due to scarceness of space and lesser importance.

8.3 Future work

One can divide the suggestions of future work into two different major categories, being the first comprised by the ones already started in this project and some times not fully applied due to tight schedule and the second constituted by completely different approaches to the topic or different applications of the CPA EoS.

Regarding the first of them, and in spite of the accomplishments of this project in greatly increasing the number of species studied, an even broader database should be created in future works, since some of the most important chemical families were still completely absent or poorly represented. Secondly, it would be very interesting to test how the pure compounds' correlations found would perform in a completely different database with only new compounds and evaluate the results in predicting vapour pressure and liquid density. Lastly, although some correlations were studied for binary mixtures with the Hudson-McCoubrey theory, it is still needed to further evaluate how well they could predict the parameters in similar compounds and how accurately those parameters could describe VLE and liquid-liquid equilibria (LLE).

To what concerns the latter category, even though it would require long research and subsequent works, it would be of great relevance to study how the CPA EoS models the behaviour of electrolytes and of ionic liquids, i.e., a particularly interesting kind of novel solvents. Moreover, further studies need to be done so as to be able of more accurately modelling species with fluorine atoms in their chemical structure. Finally, the addition of machine learning to the process of finding correlations and of predicting parameters and properties could be groundbreaking.

8.4 Final assessment

The development of this project allowed both psychological and academic growths, with self-organisation and desire of perfection teaming up with hard work and dedication to ensure the fulfilment of the project's objectives and deadlines. Notwithstanding the fact that a self-evaluation is always difficult to conceive, especially in such long projects, it is believed that, probably because of the great interest in the topic, very strong focus and commitment were kept throughout the semester and that a very good final outcome was achieved.

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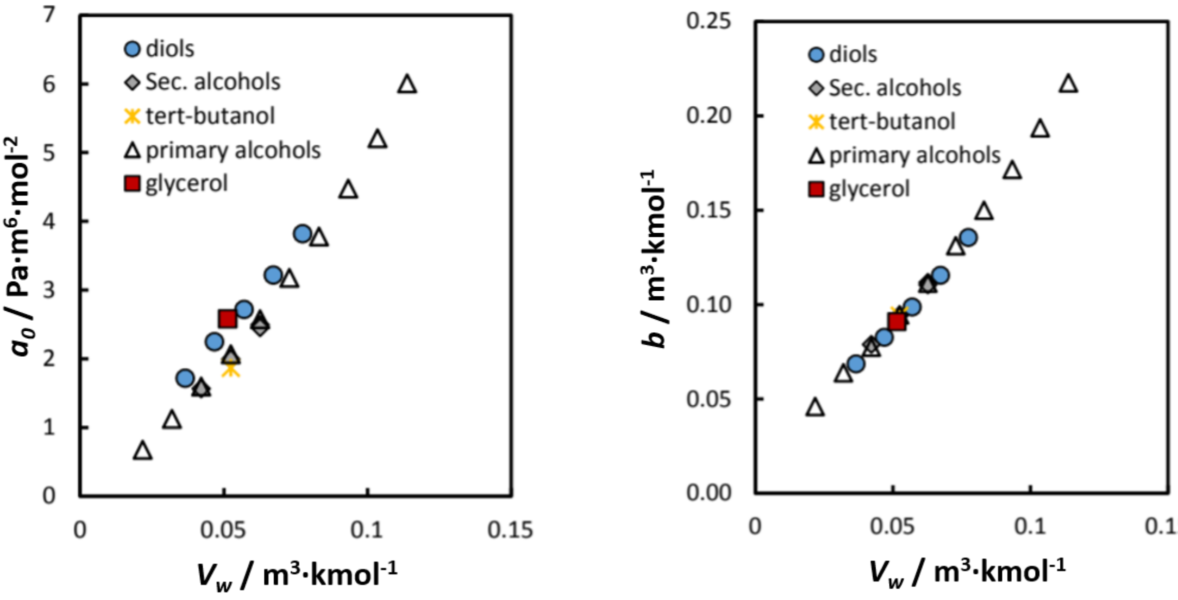
Appendix A

Figures from the literature

In this appendix, all the figures referred in the State of the Art and related to previous works in enlarging the predictability of the Cubic Plus Association equation of state can be found.



(a) Energy parameter.

(b) Co-volume parameter.

Fig. A.1: Studies of dependence of the energy parameter, a_0, and of the co-volume parameter, b, with the van der Waals volume, V_w. Reprinted and adapted from Palma *et al.* [1].

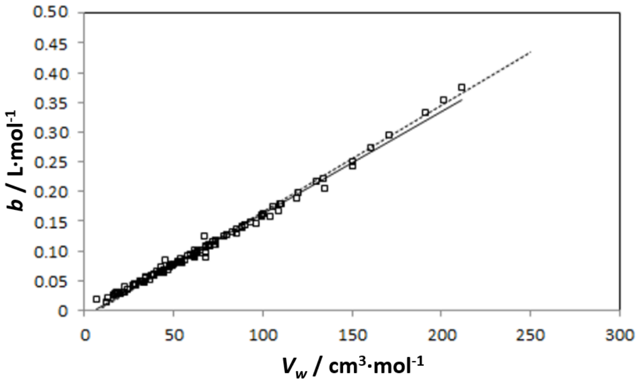


Fig. A.2: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_{w}. Reprinted and adapted from Schlaikjer [2].

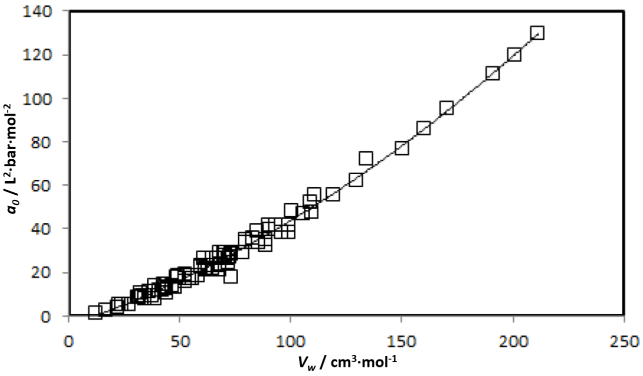


Fig. A.3: Study of dependence of the energy parameter, a_0, with the van der Waals volume, V_{w}. The regression (–) follows equation $a_0 = 0.0014 \cdot V_{\mathrm{w}}^2 + 0.3437 \cdot V_{\mathrm{w}} - 4.2829$, with a determination coefficient of 0.9938. Reprinted and adapted from Schlaikjer [2].

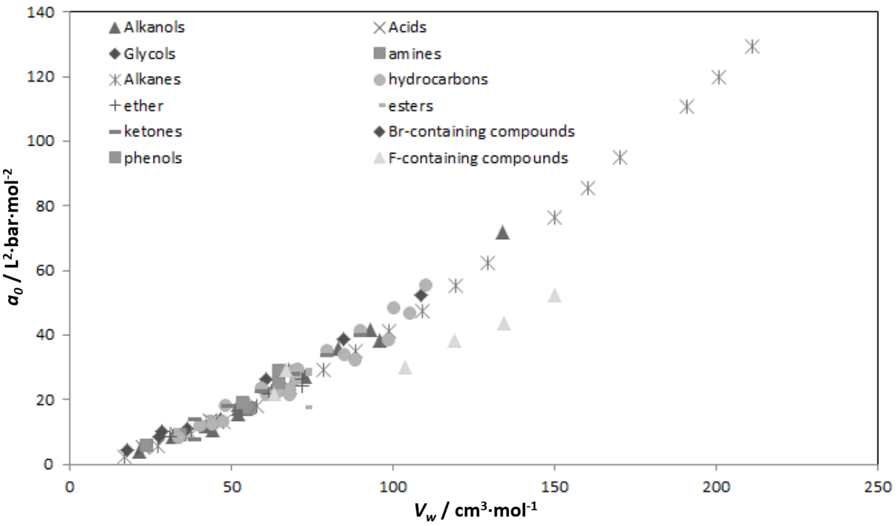


Fig. A.4: Study of dependence of the energy term parameter, a_0, with the van der Waals volume, V_{w}, by chemical family. Reprinted and adapted from Schlaikjer [2].

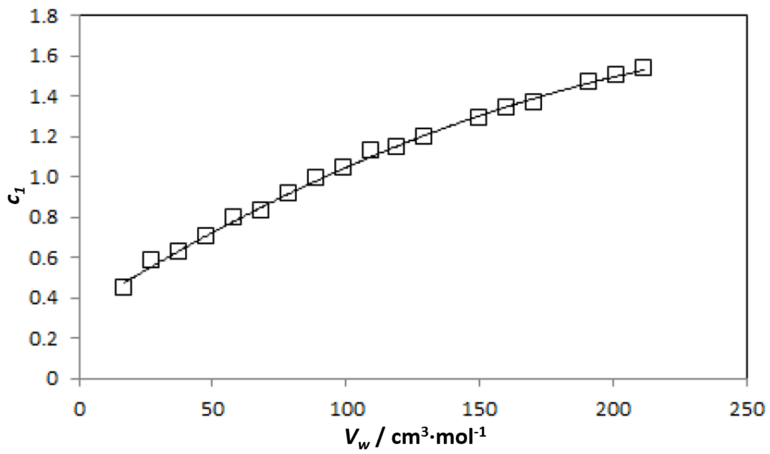


Fig. A.5: Study of dependence of the energy term parameter, c_1, with the van der Waals volume, V_w, for n-alkanes. Reprinted and adapted from Schlaikjer [2].

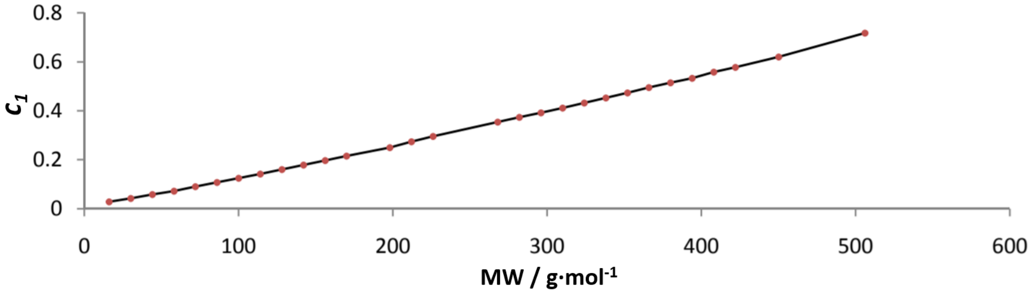


Fig. A.6: Study of dependence of the energy term parameter, c_1, with the molecular mass, MM, in some hydrocarbons. Reprinted and adapted from Ali [3].

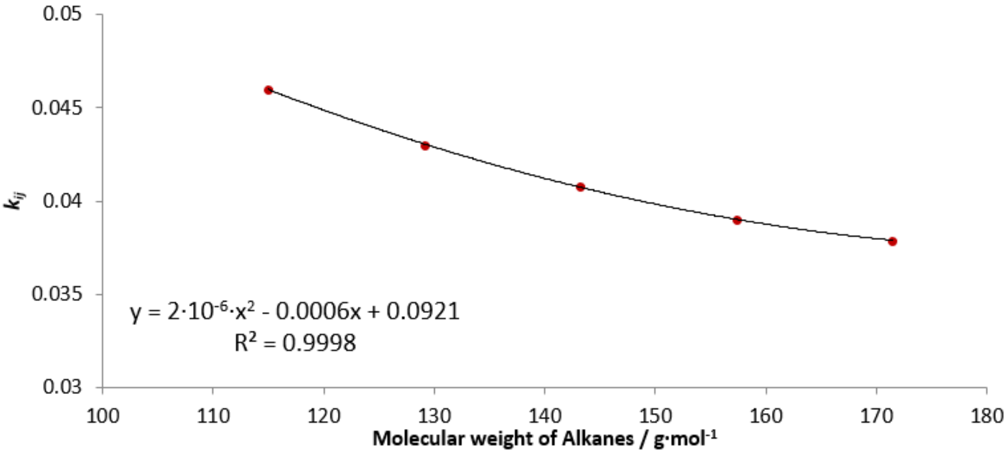


Fig. A.7: Study of dependence of the binary interaction parameter, k_{ij}, with the molecular mass for acetic acid-alkanes. Reprinted and adapted from Ali [3].

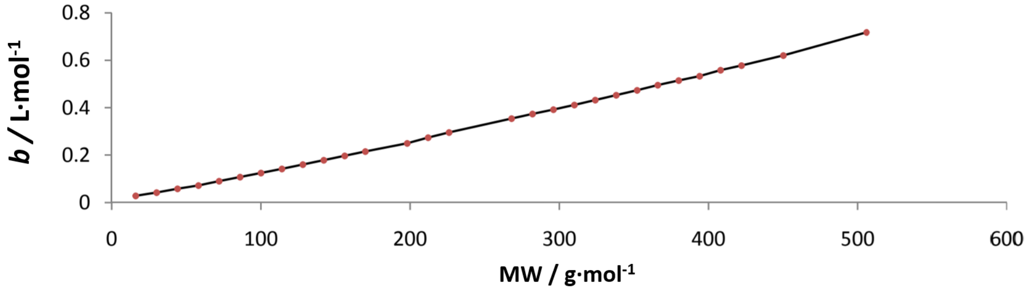


Fig. A.8: Study of dependence of the co-volume parameter, *b*, with the molecular mass, MM, in some hydrocarbons. Reprinted and adapted from Ali [3].

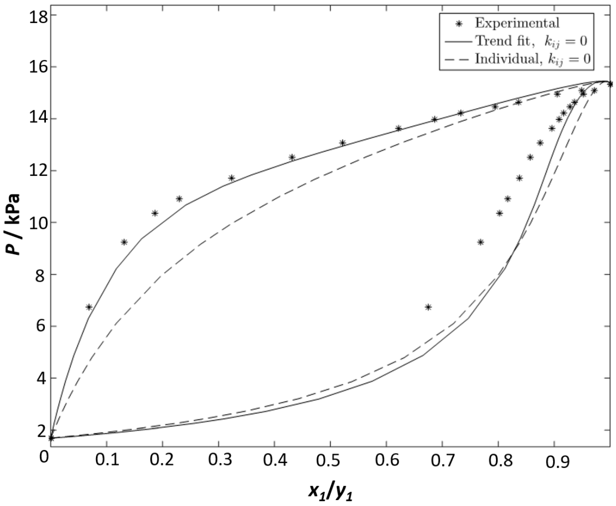


Fig. A.9: Vapour liquid equilibrium of hexane (1) and propylamine (2) at *T* = 348.15 K, where "✻" represents the experimental values, "—" the lines obtained from the trend fit method and "- -" the ones derived from the individual parameter fitting method. Reprinted and adapted from Hansen [4].

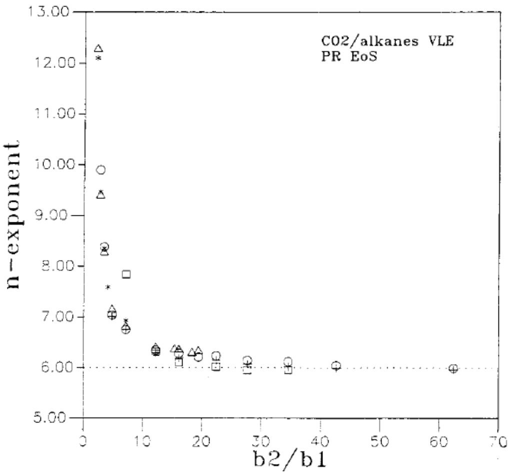


Fig. A.10: Study of dependence of the exponent *n* with the ratio of van der Waals volumes in carbon dioxide-alkanes. Reprinted from Coutinho *et al.* [5].

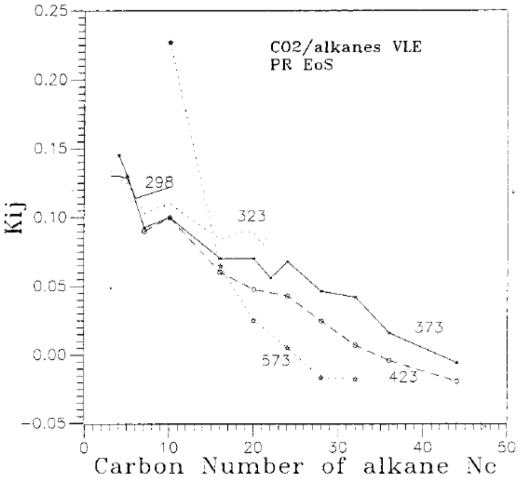


Fig. A.11: Study of dependence of the binary interaction parameter, k_{ij}, with the number of structural carbons in carbon dioxide-alkanes. Reprinted from Coutinho *et al.* [5].

A.1 Bibliography

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Appendix B

UNIFAC parameters

In this appendix, the UNIFAC, i.e., UNIversal quasichemical Functional group Activity Coefficients, groups and subgroups are presented, from Table B.1 to B.5, as well as their relative van der Waals molecular volume contribution, *R*, and their relative van der Waals molecular surface area contribution, *Q*, from Tables B.6 and B.8, needed for group contribution (GC) calculations [1].

B.1 Table of parameters

Table B.1: UNIFAC group numbers and relative van der Waals molecular volume and surface area contributions - part 1 of 5 [1].

Group number	Subgroup name	Main group	*R*	*Q*
1	CH_3	[1] CH_2	0.9011	0.8480
2	CH_2	[1] CH_2	0.6744	0.5400
3	CH	[1] CH_2	0.4469	0.2280
4	C	[1] CH_2	0.2195	0.0000
5	CH_2=CH	[2] C=C	1.3454	1.1760
6	CH=CH	[2] C=C	1.1167	0.8670
7	CH_2=C	[2] C=C	1.1173	0.9880
8	CH=C	[2] C=C	0.8886	0.6760
9	ACH	[3] ACH	0.5313	0.4000

Table B.2: UNIFAC group numbers and relative van der Waals molecular volume and surface area contributions - part 2 of 5 [1].

Group number	Subgroup name	Main group	*R*	*Q*
10	AC	[3] ACH	0.3652	0.1200
11	$\mathrm{ACCH_3}$	[4] $\mathrm{ACCH_2}$	1.2663	0.9680
12	$\mathrm{ACCH_2}$	[4] $\mathrm{ACCH_2}$	1.0396	0.6600
13	ACCH	[4] $\mathrm{ACCH_2}$	0.8121	0.3480
14	OH	[5] OH	0.5300	0.5840
15	$\mathrm{CH_3OH}$	[6] $\mathrm{CH_3OH}$	1.4311	1.4320
16	$\mathrm{H_2O}$	[7] $\mathrm{H_2O}$	0.9200	1.4000
17	ACOH	[8] ACOH	0.8952	0.6800
18	$\mathrm{CH_3CO}$	[9] $\mathrm{CH_2CO}$	1.6724	1.4880
19	$\mathrm{CH_2CO}$	[9] $\mathrm{CH_2CO}$	1.4457	1.1800
20	CHO	[10] CHO	0.9980	0.9480
21	$\mathrm{CH_3COO}$	[11] CCOO	1.9031	1.7280
22	$\mathrm{CH_2COO}$	[11] CCOO	1.6764	1.4200
23	HCOO	[12] HCOO	1.2420	1.1880
24	$\mathrm{CH_3O}$	[13] $\mathrm{CH_2O}$	1.1450	1.0880
25	$\mathrm{CH_2O}$	[13] $\mathrm{CH_2O}$	0.9183	0.7800
26	CHO	[13] $\mathrm{CH_2O}$	0.6908	0.4680
27	THF	[13] $\mathrm{CH_2O}$	0.9183	1.1000
28	$\mathrm{CH_3NH_2}$	[14] $\mathrm{CNH_2}$	1.5959	1.5440
29	$\mathrm{CH_2NH_2}$	[14] $\mathrm{CNH_2}$	1.3692	1.2360
30	$\mathrm{CHNH_2}$	[14] $\mathrm{CNH_2}$	1.1417	0.9240
21	$\mathrm{CH_3COO}$	[11] CCOO	1.9031	1.7280
22	$\mathrm{CH_2COO}$	[11] CCOO	1.6764	1.4200
23	HCOO	[12] HCOO	1.2420	1.1880
24	$\mathrm{CH_3O}$	[13] $\mathrm{CH_2O}$	1.1450	1.0880
25	$\mathrm{CH_2O}$	[13] $\mathrm{CH_2O}$	0.9183	0.7800
26	CHO	[13] $\mathrm{CH_2O}$	0.6908	0.4680
27	THF	[13] $\mathrm{CH_2O}$	0.9183	1.1000
28	$\mathrm{CH_3NH_2}$	[14] $\mathrm{CNH_2}$	1.5959	1.5440
29	$\mathrm{CH_2NH_2}$	[14] $\mathrm{CNH_2}$	1.3692	1.2360
30	$\mathrm{CHNH_2}$	[14] $\mathrm{CNH_2}$	1.1417	0.9240
31	$\mathrm{CH_3NH}$	[15] CNH	1.4337	1.2440

Table B.3: UNIFAC group numbers and relative van der Waals molecular volume and surface area contributions - part 3 of 5 [1].

Group number	Subgroup name	Main group	*R*	*Q*
32	CH_2NH	[15] CNH	1.2070	0.9360
33	CHNH	[15] CNH	0.9795	0.6240
34	CH_3N	[16] $(C)_3N$	1.1865	0.9400
35	CH_2N	[16] $(C)_3N$	0.9597	0.6320
36	$ACNH_2$	[17] $ACNH_2$	1.0600	0.8160
37	C_5H_5N	[18] Pyridine	2.9993	2.1130
38	C_5H_4N	[18] Pyridine	2.8332	1.8330
39	C_5H_3N	[18] Pyridine	2.6670	1.5530
40	CH_3CN	[19] CCN	1.8701	1.7240
41	CH_2CN	[19] CCN	1.6434	1.4160
42	COOH	[20] COOH	1.3013	1.2240
43	HCOOH	[20] COOH	1.5280	1.5320
44	CH_2Cl	[21] CCl	1.4654	1.2640
45	CHCl	[21] CCl	1.2380	0.9520
46	CCl	[21] CCl	1.0106	0.7240
47	CH_2Cl_2	[22] CCl_2	2.2564	1.9880
48	$CHCl_2$	[22] CCl_2	2.0606	1.6840
49	CCl_2	[22] CCl_2	1.8016	1.4480
50	$CHCl_3$	[23] CCl_3	2.8700	2.4100
51	CCl_3	[23] CCl_3	2.6401	2.1840
52	CCl_4	[24] CCl_4	3.3900	2.9100
53	ACCl	[25] ACCl	1.1562	0.8440
54	CH_3NO_2	[26] CNO_2	2.0086	1.8680
55	CH_2NO_2	[26] CNO_2	1.7818	1.5600
56	$CHNO_2$	[26] CNO_2	1.5544	1.2480
57	$ACNO_2$	[27] $ACNO_2$	1.4199	1.1040
58	CS_2	[28] CS_2	2.0570	1.6500
59	CH_3SH	[29] CH_3SH	1.8770	1.6760
60	CH_2SH	[29] CH_3SH	1.6510	1.3680
61	Furfural	[30] Furfural	3.1680	2.4840
62	Ethanediol	[31] Ethanediol	2.4088	2.2480
63	I	[32] I	1.2640	0.9920

Table B.4: UNIFAC group numbers and relative van der Waals molecular volume and surface area contributions - part 4 of 5 [1].

Group number	Subgroup name	Main group	***R***	***Q***
64	Br	[33] Br	0.9492	0.8320
65	CH=-C	[34] C=-C	1.2920	1.0880
66	C=-C	[34] C=-C	1.0613	0.7840
67	Dimethylsulphoxide	[35] Dimethylsulphoxide	2.8266	2.4720
68	Acrylonitrile	[36] Acrylonitrile	2.3144	2.0520
69	Cl-(C=C)	[37] ClCC	0.7910	0.7240
70	C=C	[2] C=C	0.6605	0.4850
71	ACF	[38] ACF	0.6948	0.5240
72	N,n-dimethylformamide	[39] N,n-dimethylformamide	3.0856	2.7360
73	HCON	[39] N,n-dimethylformamide	2.6322	2.1200
74	CF_3	[40] CF_2	1.4060	1.3800
75	CF_2	[40] CF_2	1.0105	0.9200
76	CF	[40] CF_2	0.6150	0.4600
77	COO	[41] COO	1.3800	1.2000
78	SiH_3	[42] SiH_2	1.6035	1.2632
79	SiH_2	[42] SiH_2	1.4443	1.0063
80	SiH	[42] SiH_2	1.2853	0.7494
81	Si	[42] SiH_2	1.0470	0.4099
82	SiH_2O	[43] SiO	1.4838	1.0621
83	SiHO	[43] SiO	1.3030	0.7639
84	SiO	[43] SiO	1.1044	0.4657
85	N-methylpyrrolidone	[44] N-methylpyrrolidone	3.9810	3.2000
86	CCl_3F	[45] CClF	3.0356	2.6440
87	CCl_2F	[45] CClF	2.2287	1.9160
88	$HCCl_2F$	[45] CClF	2.4060	2.1160
89	HCClF	[45] CClF	1.6493	1.4160
90	$CClF_2$	[45] CClF	1.8174	1.6480
91	$HCClF_2$	[45] CClF	1.9670	1.8280
92	$CClF_3$	[45] CClF	2.1721	2.1000
93	CCl_2F_2	[45] CClF	2.6243	2.3760
94	AMH_2	[46] CON(AM)	1.4515	1.2480
95	$AMHCH_3$	[46] CON(AM)	2.1905	1.7960

Table B.5: UNIFAC group numbers and relative van der Waals molecular volume and surface area contributions - part 5 of 5 [1].

Group number	Subgroup name	Main group	*R*	*Q*
96	AMHCH$_2$	[46] CON(AM)	1.9637	1.4880
97	AM(CH$_3$)$_2$	[46] CON(AM)	2.8589	2.4280
98	AMCH$_3$CH$_2$	[46] CON(AM)	2.6322	2.1200
99	AM(CH$_2$)$_2$	[46] CON(AM)	2.4054	1.8120
100	C$_2$H$_5$O$_2$	[47] OCCOH	2.1226	1.9040
101	C$_2$H$_4$O$_2$	[47] OCCOH	1.8952	1.5920
102	CH$_3$S	[48] CH$_2$S	1.6130	1.3680
103	CH$_2$S	[48] CH$_2$S	1.3863	1.0600
104	CHS	[48] CH$_2$S	1.1589	0.7480
105	Morpholine	[49] Morpholine	3.4740	2.7960
106	C$_4$H$_4$S	[50] Thiophene	2.8569	2.1400
107	C$_4$H$_3$S	[50] Thiophene	2.6908	1.8600
108	C$_4$H$_2$S	[50] Thiophene	2.5247	1.5800
109	NCO	[51] NCO	1.0567	0.7320
118	(CH$_2$)$_2$SU	[55] Sulfones	2.6869	2.1200
119	CH$_2$CHSU	[55] Sulfones	2.4595	1.8080
178	Imidazol	[84] Imidazol	2.0260	0.8680
179	BTI	[85] BTI	5.7740	4.9320

B.2 List of main groups

Table B.6: UNIFAC main group numbers and respective subgroups - part 1 of 3 [1].

Number	Main group name	Subgroups
1	CH$_2$	[1] CH$_3$, [2] CH$_2$, [3] CH, [4] C
2	C=C	[5] CH$_2$=CH, [6] CH=, [7] CH$_2$=C, [8] CH=C, [70] C=C
3	ACH	[9] ACH, [10] AC
4	ACCH$_2$	[11] ACCH$_3$, [12] ACCH$_2$, [13] ACCH
5	OH	[14] OH

Table B.7: UNIFAC main group numbers and respective subgroups - part 2 of 3 [1].

Number	Main group name	Subgroups
6	CH_3OH	[15] CH_3OH
7	H_2O	[16] H_2O
8	ACOH	[17] ACOH
9	CH_2CO	[18] CH_3CO, [19] CH_2CO
10	CHO	[20] CHO
11	CCOO	[21] CH_3COO, [22] CH_2COO
12	HCOO	[23] HCOO
13	CH_2O	[24] CH_3O, [25] CH_2O, [26] CHO, [27] THF
14	CNH_2	[28] CH_3NH_2, [29] CH_2NH_2, [30] $CHNH_2$
15	CNH	[31] CH_3NH, [32] CH_2NH, [33] CHNH
16	$(C)_3N$	[34] CH_3N, [35] CH_2N
17	$ACNH_2$	[36] $ACNH_2$
18	Pyridine	[37] C_5H_5N, [38] C_4H_2N, [39] C_5H_3N
19	CCN	[40] CH_3CN, [41] CH_2CN
20	COOH	[42] COOH, [43] HCOOH
21	CCl	[44] CH_2Cl, [45] CHCl, [46] CCl
22	CCl_2	[47] CH_2Cl_2, [48] $CHCl_2$, [49] CCl_2
23	CCl_3	[50] $CHCl_3$, [51] CCl_3
24	CCl_4	[52] CCl_4
25	ACCl	[53] ACCl
26	CNO_2	[54] CH_3NO_2, [55] CH_2NO_2, [56] $CHNO_2$
27	$ACNO_2$	[57] $ACNO_2$
28	CS_2	[58] CS_2
29	CH_3SH	[59] CH_3SH, [60] CH_2SH
30	Furfural	[61] Furfural
31	Ethanediol	[62] Ethanediol
32	I	[63] I
33	Br	[64] Br
34	C=-C	[65] CH=-C, [66]C=-C
35	Dimethylsulphoxide	[67] Dimethylsulphoxide
36	Acrylonitrile	[68] Acrylonitrile
37	ClCC	[69] Cl-(C=C)

Table B.8: UNIFAC main group numbers and respective subgroups - part 3 of 3 [1].

Number	Main group name	Subgroups
38	ACF	[71] ACF
39	N,n-dimethylformamide	[72] N,n-dimethylformamide, [73] HCON
40	CF2	[74] CF_3, [75] CF_2, [76] CF
41	COO	[77] COO
42	SIH_2	[78] SIH_3, [79] SIH_2, [80] SIH, [81] SI
43	SIO	[82] SIH_2O, [83] SIHO, [84] SIO
44	N-methylpyrrolidone	[85] N-methylpyrrolidone
45	CClF	[86] CCl_3F, [87] CCl_2F, [88] $HCCl_2F$, [89] HCClF, [90] $CClF_2$, [91] $HCClF_2$, [92] $CClF_3$, [93] CCl_2F_2
85	BTI	[179] BTI
46	CON(AM)	[94] AMH_2, [95] $AMHCH_3$, [96] $AMHCH_2$, [97] $AM(CH_3)_2$, [98] $AMCH_3CH_2$, [99] $AM(CH_2)_2$
47	OCCOH	[100] $C_2H_5O_2$, [101] $C_2H_4O_2$
48	CH_2S	[102] CH_3S, [103] CH_2S, [104] CHS
49	Morpholine	[105] Morpholine
50	Thiophene	[106] C_4H_4S, [107] C_4H_3S, [108] C_4H_2S
51	NCO	[109] NCO
55	Sulfones	[118] $(CH_2)_2SU$ [119] CH_2CHSU
84	Imidazol	[178] Imidazol

B.3 Bibliography

[1] Dortmund Data Bank. Parameters of the original UNIFAC model, 10th March 2020. Available at: `www.ddbst.com/published-parameters-unifac.html`.

Appendix C

Pure compounds' database

In this appendix, the database for the pure compounds' parameters is presented. The chemical compounds are sorted by alphabetical order.

From Table C.1 to C.9, the energy term parameter (a_0), the corrected energy term parameter (Γ), the co-volume (b) and the other energy term parameter (c_1) can be found for each entry. Secondly, the molecular mass (MM), the van der Waals surface area (A_w) and the van der Waals volume (V_w) are located from Table C.10 to C.18. Thirdly, the association energy parameter (ε) and the association volume (β) can be seen in Tables C.19, C.20 and C.21. Lastly, the critical temperature (T_c) and the critical pressure (P_c) can be observed from Table C.22 to C.29. All the references can be found in the respective tables.

Table C.1: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 1 of 9.

Nr	**Compound**	a_0 **/ bar·L^2·mol^{-2}**	Γ **/ K**	b **/ L·mol^{-1}**	c_1	**References**
1	1,2-propylene glycol	13.84	2465.453	0.0675	0.9372	[1-4]
2	1,3-butadiene	11.72[a]	2181.155	0.0646	0.6971	[5-8]
3	1,8-H-perfluorooctane	56.80[a]	3412.512	0.2002	1.0100	[9]
4	1-Br-perfluorooctane	55.20[a]	2825.278	0.2350	1.2900	[9]
5	1-butanol	15.69[a]	2368.592	0.0797	0.9784	[4-6,9-14]
6	1-decanol	54.54	3556.970	0.1844	1.0686	[15]

[a] a_0 calculated from Γ or vice-versa.

Table C.2: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 2 of 9.

Nr	**Compound**	a_0 **/ bar·L^2·mol^{-2}**	Γ **/ K**	b **/ L·mol^{-1}**	c_1	**References**
7	1-decene	46.58^a	3232.261	0.1733	1.0642	[5-8]
8	1-dodecanol	71.76^a	3898.786	0.2214	0.9650	[4-6,9-14]
9	1-heptanol	35.74	3273.130	0.1313	1.0110	[4-6,9-14]
10	1-hexanol	27.18^a	2950.202	0.1108	0.9805	[5,6,9-14]
11	1-hexene	21.98	2592.105^a	0.1020	0.8430	[16]
12	1-H-perfluorooctane	50.20^a	2925.392	0.2064	1.0700	[9]
13	1-octanol	41.58	3367.992	0.1485	1.1486	[4-6,9-14]
14	1-octene	33.63	2935.239^a	0.1378	0.9700	[16]
15	1-pentanol	22.76	2808.745	0.0975	0.9358	[4-6,9-14]
16	1-propanol	11.91	2234.515	0.0641	0.9171	[4-6,9-14]
17	2,2,4-trimethylpentane	32.17^a	2781.831	0.1391	0.8746	[5-8]
18	2,4-dimethylhexane	33.30	2836.753^a	0.1412	0.9276	[17]
19	2-butanol	17.32	2567.952^a	0.0811	0.8894	[4,17]
20	2-butanone	18.16	2822.081^a	0.0774	0.8476	[18]
21	2-butenal	18.99	3137.969^a	0.0728	0.8140	[19]
22	2-heptanone	33.63	3182.288^a	0.1271	1.0210	[18]
23	2-hexanone	27.93	3062.154^a	0.1097	0.9650	[18]
24	2-methyl-1-propanol	18.31	2717.777	0.0811	0.9035	[4-6,9-14]
25	2-methylheptane	34.18	2897.709^a	0.1419	0.9601	[17]
26	2-methylhexane	28.33	2731.683^a	0.1247	0.8991	[17]
27	2-methylpentane	21.22^a	2823.000	0.0904	0.7561	[5-8]
28	2-methylpropane	12.91^a	2078.622	0.0747	0.7021	[5-8]
29	2-methylpropene	12.24^a	2130.725	0.0691	0.7172	[5-8]
30	2-methylpyridine	23.25	3186.587^a	0.0877	0.8638	[20]
31	2-octanol	38.46	3172.501^a	0.1458	1.1689	[18]
32	2-octanone	39.87	3329.674^a	0.1440	1.0432	[18]

[a] a_0 calculated from Γ or vice-versa.

Table C.3: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 3 of 9.

Nr	**Compound**	a_0 / **bar·L^2·mol^{-2}**	Γ / **K**	b / **L·mol^{-1}**	c_1	**References**
33	2-pentanone	22.58	2919.838^a	0.0930	0.9127	[18]
34	2-propanol	10.60	1989.060	0.0641	0.9468	[5,6,9-14,17]
35	3-methylpentane	23.04^a	2607.083	0.1063	0.7996	[5-8]
36	4-methyloctane	38.26^a	2923.125	0.1574	0.9439	[5-8]
37	acetic acid	9.12	2343.797	0.0468	0.4644	[4.21]
38	acetic anhydride	23.31	3212.876	0.0873	1.0332	[4,7,12,13,22]
39	acetone	7.86^a	1597.822	0.0592	0.9951	[7,12,13,22]
40	benzaldehyde	27.84	3592.169^a	0.0932	0.8814	[13]
41	benzene	17.88^a	2867.193	0.0750	0.7576	[5-8,16]
42	benzoic acid	31.82	3765.182^a	0.1017	1.3670	[18]
43	benzyl alcohol	29.14	3602.110	0.0973	0.7533	[5,6,9-14]
44	bis(chloromethyl)ether	19.26	3017.532^a	0.0768	0.8885	[20]
45	bromine	10.25^a	2895.867	0.0426	0.6361	[23]
46	butanal	16.68	2646.262^a	0.0758	0.8803	[19]
47	butylamine	16.83	2407.490^a	0.0841	0.7580	[20]
48	butylbenzene	41.30^a	3439.614	0.1444	0.9618	[5-8]
49	carbon dioxide	3.50	1551.222	0.0273	0.7602	[24]
50	carbonyl sulfide	6.38^a	1915.170	0.0401	0.5981	[7,12,13,22]
51	cyanogenchloride	8.44	2450.768^a	0.0414	0.7641	[20]
52	cyclohexane	21.26^a	2828.913	0.0904	0.7427	[5,6,9-14]
53	diethanolamine	20.94	2669.575^a	0.0944	1.5743	[17]
54	diethyl ether	16.40	2394.135^a	0.0824	0.8481	[25]
55	diethylamine	17.25	2420.458	0.0857	0.8838	[4,11]
56	diethylene glycol	26.41	3448.783	0.0921	0.7991	[1-4]
57	diisopropyl ether	24.34	2528.086	0.1158	0.9490	[4,14,27]
58	dimethyl carbonate	17.57	2891.209^a	0.0731	0.8937	[28]

[a] a_0 calculated from Γ or vice-versa.

Table C.4: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 4 of 9.

Nr	**Compound**	a_0 **/ bar·L^2·mol^{-2}**	Γ **/ K**	b **/ L·mol^{-1}**	c_1	**References**
59	dimethyl disulfide	19.63[a]	3082.820	0.0766	0.7992	[7,12,13,22]
60	dimethyl ether	8.44	2045.568	0.0496	0.7213	[4,14,27]
61	dimethyl sulfide	12.63[a]	2578.930	0.0589	0.7213	[7,12,13,22]
62	di-n-propyl-ether	26.38	2740.257[a]	0.1158	0.9296	[25]
63	dipropyl ether	26.38	2740.887	0.1158	0.9296	[4,14,27]
64	ethane	5.51[a]	1544.548	0.0429	0.5846	[5,6,29]
65	ethanol	8.67	2123.828	0.0491	0.7369	[4-6,9-14]
66	ethyl benzene	28.86	3193.248[a]	0.1087	0.8539	[16]
67	ethyl butyrate	29.44	3052.533[a]	0.1160	0.9103	[30]
68	ethyl decanoate	70.40	3927.261[a]	0.2156	1.2163	[30]
69	ethyl dodecanoate	83.11	4020.851[a]	0.2486	1.2817	[30]
70	ethyl ethanoate	18.88	2723.517	0.0834	0.9427	[4,14,27]
71	ethyl hexadecanoate	104.70	3962.403[a]	0.3178	1.5770	[30]
72	ethyl isopentanoate	33.19	2996.606[a]	0.1332	1.0422	[30]
73	ethyl mercaptan	12.42[a]	2548.920	0.0586	0.7221	[7,12,13,22]
74	ethyl methanoate	5.63	2151.512	0.0300	0.3338	[4,21]
75	ethyl octanoate	57.73	3800.396[a]	0.1827	1.1336	[30]
76	ethyl propanoate	23.09	2797.029[a]	0.0993	1.0334	[30]
77	ethyl propyl ether	21.77	2609.032	0.1003	0.8498	[4,14,27]
78	ethyl tetradecanoate	90.70	3866.963[a]	0.2821	1.4865	[30]
79	ethylamine	9.06	2051.471	0.0531	0.7382	[4,11]
80	ethylbenzene	28.86[a]	3192.838	0.1087	0.8539	[5-8]
81	ethylcyclohexane	32.33	3120.764[a]	0.1246	0.8247	[17]
82	glycerol	11.80	2010.218[a]	0.0706	1.1800	[30]
83	hexafluorobenzene	21.80	2680.918[a]	0.0978	0.9900	[17]
84	hexylbenzene	55.33[a]	3692.217	0.1802	1.0436	[5-8]

[a] a_0 calculated from Γ or vice-versa.

Table C.5: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 5 of 9.

Nr	**Compound**	a_0 / $\mathbf{bar \cdot L^2 \cdot mol^{-2}}$	Γ / **K**	b / $\mathbf{L \cdot mol^{-1}}$	c_1	**References**
85	hydrogen bromide	4.39[a]	1805.656	0.0292	0.6005	[23]
86	hydrogen sulfide	3.86	1590.102	0.0285	0.5022	[24]
87	i-butyl acetate	28.08[a]	2903.549	0.1163	1.0389	[4,14,27]
88	indole	35.61	4206.832[a]	0.1018	0.9411	[20]
89	isobutanal	16.89	2639.268[a]	0.0770	0.9128	[20]
90	isobutane	12.91	2078.506[a]	0.0747	0.7021	[17]
91	isobutanol	18.31	2717.626[a]	0.0811	0.9035	[17]
92	m-cresol	28.41[a]	3503.432	0.0975	0.8207	[14]
93	methane	2.32[a]	959.028	0.0291	0.4472	[5,6,29]
94	methanol	4.05	1573.707	0.0310	0.4310	[4-6,9-14]
95	methyl bromide	8.58[a]	2354.785	0.0438	0.6693	[23]
96	methyl butyl ether	21.45	2635.242[a]	0.0979	0.8870	[25]
97	methyl butyrate	23.31	2851.666[a]	0.0983	0.9974	[30]
98	methyl decanoate	59.00	3499.048[a]	0.2028	1.3097	[30]
99	methyl diethanolamine	21.66	2337.352[a]	0.1115	1.3371	[17]
100	methyl dodecanoate	74.36	3723.486[a]	0.2402	1.3768	[30]
101	methyl ethanoate	14.59	2649.496	0.0663	0.8719	[4,14,27]
102	methyl heptanoate	40.53	3309.327[a]	0.1473	1.1290	[30]
103	methyl hexadecanoate	105.05	4004.593[a]	0.3155	1.5496	[30]
104	methyl hexanoate	34.60	3176.659[a]	0.1310	1.0853	[30]
105	methyl mercaptan	8.23[a]	2266.270	0.0437	0.8007	[7,12,13,22]
106	methyl methacrylate	22.27	2892.446[a]	0.0926	0.9145	[25]
107	methyl methanoate	10.52	2528.212	0.0501	0.7962	[4,14,27]
108	methyl nonanoate	55.53	3718.666[a]	0.1796	1.0968	[30]
109	methyl octadecanoate	122.59	4190.900[a]	0.3518	1.5966	[31]
110	methyl octanoate	47.06	3438.650[a]	0.1646	1.1552	[30]

[a] a_0 calculated from Γ or vice-versa.

Table C.6: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 6 of 9.

Nr	**Compound**	a_0 **/ bar·L^2·mol^{-2}**	Γ **/ K**	b **/ L·mol^{-1}**	c_1	**References**
111	methyl oleate	107.00	3854.191^a	0.3339	1.8600	[32]
112	methyl pentadecanoate	96.06	4151.406^a	0.2783	1.3268	[30]
113	methyl pentanoate	29.51	3094.366^a	0.1147	0.9976	[30]
114	methyl propanoate	18.48	2714.425^a	0.0819	0.9670	[30]
115	methyl tetradecanoate	87.97	3803.278^a	0.2782	1.4744	[30]
116	methyl tridecanoate	78.41	3841.367^a	0.2455	1.3667	[30]
117	methyl undecanoate	66.80	3779.019^a	0.2126	1.2451	[30]
118	methylamine	5.49	1828.708	0.0361	0.6044	[4,11]
119	methylcyclohexane	26.45^a	2926.373	0.1087	0.7766	[5-8]
120	monoethanolamine	12.14^a	2675.100	0.0546	0.8316	[33]
121	monoethylene glyco	10.82	2531.710	0.0514	0.6744	[1-4]
122	m-xylene	29.09	3217.841	0.1087	0.8681	[5-8,16]
123	n-butane	13.14	2193.083	0.0721	0.7077	[5,6,29]
124	n-butyl acetate	29.24	2962.065	0.1189	0.9780	[4,14,27]
125	n-butyl butyrate	40.37	3223.715^a	0.1506	1.0704	[30]
126	n-butyl ethanoate	29.24	2982.530^a	0.1179	1.0250	[30]
127	n-butyl mercaptan	21.94^a	2859.510	0.0923	0.8916	[7,12,13,22]
128	n-butyl methanoate	24.02	2905.775^a	0.0994	0.9629	[30]
129	n-butyl nonanoate	76.30	3784.190^a	0.2425	1.1315	[30]
130	n-butyl octadecanoate	138.44	4054.177^a	0.4107	1.7166	[30]
131	n-butyl pentanoate	46.66	3316.731^a	0.1692	1.1811	[30]
132	n-butyl propanoate	33.90	3063.286^a	0.1331	1.1038	[30]
133	n-decane	47.39	3190.542	0.1787	1.1324	[4-6,29]
134	n-docosane	149.41	4360.786^a	0.4121	1.5955	[31]
135	n-dodecane	62.40	3471.038	0.2162	1.1953	[4-6,29]
136	n-dotriacontane	247.55	4799.847^a	0.6203	1.9650	[31]

[a] a_0 calculated from Γ or vice-versa.

Table C.7: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 7 of 9.

Nr	**Compound**	a_0 / **bar·L^2·mol^{-2}**	Γ / **K**	b / **L·mol^{-1}**	c_1	**References**
137	n-eicosane	129.53	4161.435	0.3744	1.5367	[4-6,29]
138	n-heneicosane	140.35	4307.447^a	0.3919	1.5598	[31]
139	n-heptacosane	196.10	4586.518^a	0.5142	1.8080	[31]
140	n-heptane	29.18	2799.762	0.1254	0.9137	[4-6,29]
141	n-hexacosane	186.53	4532.114^a	0.4950	1.7562	[31]
142	n-hexadecane	94.91	3855.510	0.2961	1.3728	[4-6,29]
143	n-hexane	23.68	2640.030	0.1079	0.8313	[4-6,29]
144	n-hexatriacontane	302.39	5067.825^a	0.7177	1.9928	[31]
145	nitrobenzene	32.61	3986.108^a	0.0984	0.8447	[20]
146	nitrogen	1.37^a	634.070	0.0261	0.4986	[7,12,13,22]
147	n-nonacosane	216.91	4677.139^a	0.5578	1.8641	[31]
148	n-nonadecane	119.72	4069.154	0.3539	1.5084	[4-6,29]
149	n-nonane	41.25	3094.221	0.1604	1.0463	[4-6,29]
150	n-octacosane	205.49	4632.465^a	0.5335	1.9331	[31]
151	n-octadecane	110.81	3994.222	0.3337	1.4698	[4-6,29]
152	n-octane	34.88	2944.911	0.1424	0.9942	[4-6,29]
153	n-pentacosane	175.60	4465.253^a	0.4730	1.7282	[31]
154	n-pentadecane	85.64^a	3751.990	0.2745	1.3404	[5,6,29]
155	n-pentane	18.20	2405.105	0.0910	0.7986	[4-6,29]
156	n-perfluoroheptane	38.20^a	2431.037	0.1890	1.2100	[9]
157	n-perfluorohexane	29.90^a	2261.851	0.1590	1.2000	[9]
158	n-perfluorononane	52.30^a	2599.419	0.2420	1.4200	[9]
159	n-perfluorooctane	43.70^a	2551.551	0.2060	1.3200	[9]
160	n-propyl butyrate	34.38	3088.009^a	0.1339	1.0333	[30]
161	n-propyl ethanoate	23.63	2844.399^a	0.0999	1.0450	[30]
162	n-propyl mercaptan	16.93^a	2671.420	0.0762	0.8398	[7,12,13,22]

^{a} a_0 calculated from Γ or vice-versa.

Table C.8: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 8 of 9.

Nr	**Compound**	a_0 / bar·L^2·mol^{-2}	Γ / K	b / L·mol^{-1}	c_1	**References**
163	n-propyl methanoate	18.98	2756.242^a	0.0828	0.9189	[30]
164	n-propyl propanoate	28.80	2975.398^a	0.1164	1.0161	[30]
165	n-tetracosane	166.65	4421.173^a	0.4534	1.6792	[31]
166	n-tetradecane	76.62	3678.418	0.2505	1.2906	[4-6,29]
167	n-triacontane	226.98	4725.536^a	0.5777	1.8977	[31]
168	n-tricosane	155.92	4336.310^a	0.4325	1.6680	[31]
169	n-undecane	55.22	3357.694	0.1979	1.1437	[4-6,29]
170	o-cresol	24.98^a	3135.313	0.0958	0.8960	[14]
171	octafluorotoluene	29.00	1742.207^a	0.2002	1.0400	[17]
172	oxygen	1.39	773.974	0.0216	0.4754	[7,12,13,22]
173	o-xylene	29.20	3233.843^a	0.1086	0.8800	[34]
174	p-cresol	28.84^a	3567.672	0.0972	0.8298	[14]
175	pentylbenzene	48.42^a	3601.973	0.1617	0.9795	[5-8]
176	perfluorodecalin	86.40^a	2422.403	0.4290	1.3800	[9]
177	perfluoromethylcyclohexane	35.00^a	2584.264	0.1629	0.9600	[9]
178	perfluorotoluene	29.00^a	2812.978	0.1240	1.0400	[9]
179	phenol	18.84^a	2829.035	0.0801	0.9087	[14]
180	propane	9.12	1896.453	0.0578	0.6307	[4-6,29]
181	propionic acid	13.27	2489.570	0.0641	0.6891	[4,21]
182	propylbenzene	34.82^a	3301.724	0.1269	0.9117	[5-8]
183	propylene	8.07 ^{a}	1834.800	0.0529	0.6777	[5-8]
184	p-xylene	29.32	3211.454	0.1098	0.8626	[4-8]
185	pyridine	18.85	3166.481^a	0.0716	0.7706	[20]
186	s-trioxane	16.96	3118.109^a	0.0654	0.8773	[20]
187	sulfuryl chloride	15.97	2808.092^a	0.0684	0.7579	[20]
188	terephthalic acid	54.56	4860.105	0.1350^a	1.4845	[18]

^{a} a_0 calculated from Γ or vice-versa.

Table C.9: Energy term parameter (a_0), corrected energy parameter (Γ), co-volume (b) and energy term parameter (c_1) for each compound in the database - part 9 of 9.

Nr	**Compound**	a_0 **/ bar·L²·mol⁻²**	Γ **/ K**	b **/ L·mol⁻¹**	c_1	**References**
189	tert-butanol	17.15[a]	2531.000	0.0815	0.9614	[5,6,9-14]
190	tert-butyl mercaptan	20.11[a]	2587.010	0.0935	0.8140	[7,12,13,22]
191	tetraethylene glycol	48.63	3789.490	0.1666	1.5911	[1-4]
192	tetrahydrothiophene	18.80	2902.811	0.0779[a]	0.5831	[20]
193	toluene	23.38[a]	3051.360	0.0921	0.8037	[5-8]
194	trichloromethan	15.12	2734.433	0.0665[a]	0.7454	[17]
195	triethylamine	19.50	2022.954	0.1160[a]	0.7821	[20]
196	triethylene glycol	39.13	3622.490	0.1289	0.9676	[1-4]
197	water	1.23	1017.338	0.0145	0.6736	[17,35]

[a] a_0 calculated from Γ or vice-versa.

Table C.10: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 1 of 9.

Nr	**Compound**	**MM / g·mol⁻¹**	A_w**·10⁻⁹ / cm²·mol⁻¹**	V_w **/ cm³·mol⁻¹**	**Chemical Family**	**References**
1	1,2-propylene glycol	76.09	6.96	46.76	Polyols	[1-4]
2	1,3-butadiene	54.09	5.88	40.80[b]	Alkenes	[5-8]
3	1,8-H-perfluorooctane	402.08	19.54	126.08[b]	Fluorocarbons	[9]
4	1-Br-perfluorooctane	498.97	21.05	143.03	Fluorocarbons	[9]
5	1-butanol	74.12	7.63	52.40	Alcohols	[4-6,9-14]
6	1-decanol	158.28	15.73	113.79[b]	Alcohols	[15]
7	1-decene	140.27	14.51	105.69[b]	Alkenes	[5-8]
8	1-dodecanol	186.34	18.43	134.25	Alcohols	[4-6,9-14]
9	1-heptanol	116.88	11.68	83.09	Alcohols	[4-6,9-14]
10	1-hexanol	102.16	10.33	79.99[b]	Alcohols	[5,6,9-14]

[b] V_w calculated following Bondi's method. All A_w were calculated using Bondi's method.

Table C.11: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 2 of 9.

Nr	**Compound**	**MM** / $\mathbf{g \cdot mol^{-1}}$	$A_w \cdot \mathbf{10^{-9}}$ / $\mathbf{cm^2 \cdot mol^{-1}}$	V_w / $\mathbf{cm^3 \cdot mol^{-1}}$	**Chemical Family**	**References**
11	1-hexene	84.16	9.11	71.55^b	Alkenes	[16]
12	1-H-perfluorooctane	420.07	20.12	132.08^b	Fluorocarbons	[9]
13	1-octanol	130.23	13.03	93.32	Alcohols	[4-6,9-14]
14	1-octene	112.21	11.81	85.23^b	Alkenes	[16]
15	1-pentanol	88.15	8.98	62.63	Alcohols	[4-6,9-14]
16	1-propanol	60.09	6.28	42.17	Alcohols	[4-6,9-14]
17	2,2,4-trimethylpentane	114.23	12.52	88.69^b	Alkanes	[5-8]
18	2,4-dimethylhexane	114.23	12.32	88.70^b	Alkanes	[17]
19	2-butanol	74.12	7.62	52.39	Alcohols	[4,17]
20	2-butanone	72.11	6.40	44.60^b	Ketones	[18]
21	2-butenal	70.09	5.46	41.09^b	Aldehydes	[19]
22	2-heptanone	114.18	10.45	75.29^b	Ketones	[18]
23	2-hexanone	100.16	9.10	65.06^b	Ketones	[18]
24	2-methyl-1-propanol	74.12	7.62	52.39	Alcohols	[4-6,9-14]
25	2-methylheptane	114.23	12.33	88.71	Alkanes	[17]
26	2-methylhexane	100.20	10.98	78.48^b	Alkanes	[17]
27	2-methylpentane	86.18	9.63	68.25^b	Alkanes	[5-8]
28	2-methylpropane	58.12	6.93	47.79^b	Alkanes	[5-8]
29	2-methylpropene	56.11	6.71	44.29^b	Alkenes	[5-8]
30	2-methylpyridine	93.13	7.02	51.11^b	Amines	[20]
31	2-octanol	130.23	13.02	100.44^b	Alcohols	[18]
32	2-octanone	128.21	11.59	85.52^b	Ketones	[18]
33	2-pentanone	86.13	7.54	54.83^b	Ketones	[18]
34	2-propanol	60.10	6.27	45.84^b	Alcohols	[5,6,9-14,17]
35	3-methylpentane	86.18	9.63	68.25^b	Alkanes	[5-8]
36	4-methyloctane	128.25	13.68	98.94^b	Alkanes	[5-8]

^{b} V_w calculated following Bondi's method. All A_w were calculated using Bondi's method.

Table C.12: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 3 of 9.

Nr	**Compound**	**MM / g·mol^{-1}**	A_w**·10^{-9} / cm^2·mol^{-1}**	V_w **/ cm^3·mol^{-1}**	**Chemical Family**	**References**
37	acetic acid	60.05	4.89	33.41	Carboxylic acids	[4,21]
38	acetic anhydride	102.09	8.24	54.24	Anhydrides	[4,7,12,13,22]
39	acetone	58.08	4.84	34.40^b	Ketones	[7,12,13,22]
40	benzaldehyde	106.12	7.67	53.88^b	Aromatics	[13]
41	benzene	78.11	6.00	48.36^b	Aromatics	[5-8,16]
42	benzoic acid	122.12	8.07	62.25^b	Aromatics	[18]
43	benzyl alcohol	108.14	8.11	71.24^b	Aromatics	[5,6,9-14]
44	bis(chloromethyl)ether	114.96	7.70	56.18^b	Ethers	[20]
45	bromine	79.90	4.16	28.80^b	^{c}	[23]
46	butanal	72.11	5.99	44.61^b	Aldehydes	[19]
47	butylamine	73.14	7.91	54.90^b	Amines	[20]
48	butylbenzene	134.22	11.47	90.20^b	Aromatics	[5-8]
49	carbon dioxide	44.01	3.20	29.61^b	^{c}	[24]
50	carbonyl sulfide	66.08	0.43	32.05^b	Sulfides	[7,12,13,22]
51	cyanogenchloride	61.46	4.00	40.37^b	Chlorides	[20]
52	cyclohexane	84.16	8.10	61.38^b	Cycloalkanes	[5,6,9-14]
53	diethanolamine	105.14	9.31	79.34	Amines	[17]
54	diethyl ether	74.12	8.53	59.52	Ethers	[25]
55	diethylamine	73.14	7.93	55.88	Amines	[4,11]
56	diethylene glycol	106.12	9.91	60.70	Polyols	[1-4]
57	diisopropyl ether	102.18	11.42	71.94	Ethers	[4,14,27]
58	dimethyl carbonate	90.08	8.04	55.35	Esters	[28]
59	dimethyl disulfide	94.19	3.47	48.94	Sulfides	[7,12,13,22]
60	dimethyl ether	46.07	5.63	31.04	Ethers	[4,14,27]
61	dimethyl sulfide	62.13	3.86	38.14	Sulfides	[7,12,13,22]

^{b} V_w calculated following Bondi's method. ^{c} Compounds without a well-defined chemical family.

All A_w were calculated using Bondi's method.

Table C.13: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 4 of 9.

Nr	**Compound**	**MM** / g·mol^{-1}	$A_w \cdot 10^{-9}$ / cm^2·mol^{-1}	V_w / cm^3·mol^{-1}	**Chemical Family**	**References**
62	di-n-propyl-ether	102.17	10.66	79.98	Ethers	[25]
63	dipropyl ether	102.17	11.23	71.96	Ethers	[4,14,27]
64	ethane	30.07	4.24	27.34	Alkanes	[5,6,29]
65	ethanol	46.07	4.93	31.94	Alcohols	[4-6,9-14]
66	ethyl benzene	106.17	8.77	69.74	Aromatics	[16]
67	ethyl butyrate	116.16	10.49	73.23	Esters	[30]
68	ethyl decanoate	200.32	18.59	134.61	Esters	[30]
69	ethyl dodecanoate	228.37	21.29	155.07	Esters	[30]
70	ethyl ethanoate	88.11	7.79	52.77	Esters	[4,14,27]
71	ethyl hexadecanoate	284.48	26.69	195.99	Esters	[30]
72	ethyl isopentanoate	130.18	11.83	83.46	Esters	[30]
73	ethyl mercaptan	62.13	3.66	38.14	Thiols	[7,12,13,22]
74	ethyl methanoate	46.03	6.24	23.18	Esters	[4,21]
75	ethyl octanoate	172.26	15.89	114.15	Esters	[30]
76	ethyl propanoate	102.13	9.14	63.00	Esters	[30]
77	ethyl propyl ether	88.15	9.88	61.73	Ethers	[4,14,27]
78	ethyl tetradecanoate	256.42	23.99	175.53	Esters	[30]
79	ethylamine	45.08	5.21	34.44	Amines	[4,11]
80	ethylbenzene	106.17	8.77	69.74	Aromatics	[5-8]
81	ethylcyclohexane	112.21	10.79	81.83	Cycloalkanes	[17]
82	glycerol	92.09	7.65	51.36	Polyols	[30]
83	hexafluorobenzene	186.06	7.86	63.24	Fluorocarbons	[17]
84	hexylbenzene	162.27	14.17	110.66	Aromatics	[5-8]
85	hydrogen bromide	80.91	2.65	17.85	Bromides	[23]
86	hydrogen sulfide	34.10	0.76	17.70	Sulfides	[24]
87	i-butyl acetate	116.16	10.49	73.22	Esters	[4,14,27]

[b] V_w calculated following Bondi's method. All A_w were calculated using Bondi's method.

Table C.14: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 5 of 9.

Nr	**Compound**	**MM** / $\mathbf{g{\cdot}mol^{-1}}$	$A_w{\cdot}\mathbf{10^{-9}}$ / $\mathbf{cm^2{\cdot}mol^{-1}}$	V_w / $\mathbf{cm^3{\cdot}mol^{-1}}$	**Chemical Family**	**References**
88	indole	117.15	7.94	67.35^b	Aromatics	[20]
89	isobutanal	72.11	5.98	44.60^b	Aldehydes	[20]
90	isobutane	58.12	6.93	47.79^b	Alkanes	[17]
91	isobutanol	74.12	7.62	52.39^b	Alcohols	[17]
92	m-cresol	108.14	8.12	65.03^b	Aromatics	[14]
93	methane	16.04	2.69	17.12^b	Alkanes	[5,6,29]
94	methanol	32.04	3.58	21.71^b	Alcohols	[4-6,9-14]
95	methyl bromide	94.94	4.20	28.07^b	Bromides	[23]
96	methyl butyl ether	88.15	9.87	69.75^b	Ethers	[25]
97	methyl butyrate	102.13	9.14	63.00	Esters	[30]
98	methyl decanoate	186.24	17.24	124.38	Esters	[30]
99	methyl diethanolamine	119.16	10.67	89.26^b	Amines	[17]
100	methyl dodecanoate	214.24	19.94	144.84	Esters	[30]
101	methyl ethanoate	74.08	6.44	42.54	Esters	[4,14,27]
102	methyl heptanoate	144.21	13.19	93.69	Esters	[30]
103	methyl hexadecanoate	270.24	25.34	185.76	Esters	[30]
104	methyl hexanoate	130.18	11.84	83.46	Esters	[30]
105	methyl mercaptan	48.11	2.31	27.93^b	Thiols	[7,12,13,22]
106	methyl methacrylate	100.12	8.91	60.58^b	Esters	[25]
107	methyl methanoate	60.05	4.89	32.51	Esters	[4,14,27]
108	methyl nonanoate	172.24	15.89	114.15	Esters	[30]
109	methyl octadecanoate	298.24	28.04	206.22	Esters	[31]
110	methyl octanoate	158.24	14.54	103.92	Esters	[30]
111	methyl oleate	296.50	27.51	202.71^b	Esters	[32]
112	methyl pentadecanoate	256.24	23.99	175.53	Esters	[30]
113	methyl pentanoate	116.16	10.49	73.23	Esters	[30]

[b] V_w calculated following Bondi's method. All A_w were calculated using Bondi's method.

Table C.15: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 6 of 9.

Nr	**Compound**	**MM** / $g \cdot mol^{-1}$	$A_w \cdot 10^{-9}$ / $cm^2 \cdot mol^{-1}$	V_w / $cm^3 \cdot mol^{-1}$	**Chemical Family**	**References**
114	methyl propanoate	88.11	7.79	52.77	Esters	[30]
115	methyl tetradecanoate	242.24	22.64	165.30	Esters	[30]
116	methyl tridecanoate	228.24	21.29	155.07	Esters	[30]
117	methyl undecanoate	200.24	18.59	134.61	Esters	[30]
118	methylamine	31.05	3.86	24.21	Amines	[4,11]
119	methylcyclohexane	98.19	9.44	71.60[b]	Cycloalkanes	[5-8]
120	monoethanolamine	61.08	5.90	46.17[b]	Amines	[33]
121	monoethylene glycol	62.07	5.62	36.54	Polyols	[1-4]
122	m-xylene	106.16	8.84	70.66[b]	Aromatics	[5-8,16]
123	n-butane	58.12	6.94	47.80	Alkanes	[5,6,29]
124	n-butyl acetate	116.16	10.49	73.23	Esters	[4,14,27]
125	n-butyl butyrate	144.21	13.19	93.89	Esters	[30]
126	n-butyl ethanoate	116.16	10.49	73.23	Esters	[30]
127	n-butyl mercaptan	90.18	6.55	58.61[b]	Thiols	[7,12,13,22]
128	n-butyl methanoate	102.13	8.94	63.20	Esters	[30]
129	n-butyl nonanoate	214.31	19.94	144.84	Esters	[30]
130	n-butyl octadecanoate	340.49	32.09	236.91	Esters	[30]
131	n-butyl pentanoate	158.23	14.54	103.92	Esters	[30]
132	n-butyl propanoate	130.18	11.84	83.46	Esters	[30]
133	n-decane	142.28	15.04	109.18	Alkanes	[4-6,29]
134	n-docosane	310.60	31.24	231.95[b]	Alkanes	[31]
135	n-dodecane	170.33	17.74	129.65	Alkanes	[4-6,29]
136	n-dotriacontane	450.90	44.74	334.26[b]	Alkanes	[31]
137	n-eicosane	282.55	28.54	211.49	Alkanes	[4-6,29]
138	n-heneicosane	296.60	29.89	221.72[b]	Alkanes	[31]

[b] V_w calculated following Bondi's method. [c] Compounds without a well-defined chemical family.

All A_w were calculated using Bondi's method.

Table C.16: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 7 of 9.

Nr	**Compound**	**MM** / g·mol^{-1}	A_w·10^{-9} / cm^2·mol^{-1}	V_w / cm^3·mol^{-1}	**Chemical Family**	**References**
139	n-heptacosane	380.70	37.99	283.11^b	Alkanes	[31]
140	n-heptane	100.21	10.99	78.49	Alkanes	[4-6,29]
141	n-hexacosane	366.70	36.64	272.87^b	Alkanes	[31]
142	n-hexadecane	226.41	23.14	170.57	Alkanes	[4-6,29]
143	n-hexane	86.18	9.64	68.26	Alkanes	[4-6,29]
144	n-hexatriacontane	507.00	50.14	375.18^b	Alkanes	[31]
145	nitrobenzene	123.11	7.85	61.84 ^{b}	Aromatics	[20]
146	nitrogen	28.01	1.20	8.66 ^{b}	^{c}	[7,12,13,22]
147	n-nonacosane	408.80	40.69	303.57^b	Alkanes	[31]
148	n-nonadecane	268.50	27.19	201.26	Alkanes	[4-6,29]
149	n-nonane	128.20	13.69	98.95	Alkanes	[4-6,29]
150	n-octacosane	394.80	39.34	293.34^b	Alkanes	[31]
151	n-octadecane	254.50	25.84	191.03	Alkanes	[4-6,29]
152	n-octane	114.23	12.34	88.72	Alkanes	[4-6,29]
153	n-pentacosane	352.70	35.29	262.64^b	Alkanes	[31]
154	n-pentadecane	212.42	21.79	160.34^b	Alkanes	[5,6,29]
155	n-pentane	72.15	8.29	58.03	Alkanes	[4-6,29]
156	n-perfluoroheptane	388.05	18.40	119.30^b	Fluorocarbons	[9]
157	n-perfluorohexane	338.04	16.10	103.98^b	Fluorocarbons	[9]
158	n-perfluorononane	488.06	23.00	149.96^b	Fluorocarbons	[9]
159	n-perfluorooctane	438.06	20.70	134.63^b	Fluorocarbons	[9]
160	n-propyl butyrate	130.13	11.84	83.66	Esters	[30]
161	n-propyl ethanoate	102.13	9.14	63.00	Esters	[30]
162	n-propyl mercaptan	76.16	5.01	44.92^b	Thiols	[7,12,13,22]
163	n-propyl methanoate	88.11	7.59	52.97	Esters	[30]

[b] V_w calculated following Bondi's method. [c] Compounds without a well-defined chemical family.

All A_w were calculated using Bondi's method.

Table C.17: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 8 of 9.

Nr	**Compound**	**MM / g·mol^{-1}**	**$A_w \cdot 10^{-9}$ / cm^2·mol^{-1}**	**V_w / cm^3·mol^{-1}**	**Chemical Family**	**References**
164	n-propyl propanoate	116.13	10.49	73.23	Esters	[30]
165	n-tetracosane	338.70	33.94	252.41^b	Alkanes	[31]
166	n-tetradecane	198.39	20.44	150.11	Alkanes	[4-6,29]
167	n-triacontane	422.80	42.04	313.80^b	Alkanes	[31]
168	n-tricosane	324.60	32.59	242.18^b	Alkanes	[31]
169	n-undecane	156.31	16.39	119.42	Alkanes	[4-6,29]
170	o-cresol	108.14	8.12	51.36^b	Aromatics	[14]
171	octafluorotoluene	236.06	10.89	76.24	Fluorocarbons	[17]
172	oxygen	32.00	1.20	23.44	^{c}	[7,12,13,22]
173	o-xylene	106.16	8.84	70.66	Aromatics	[34]
174	p-cresol	108.14	8.12	51.36	Aromatics	[14]
175	pentylbenzene	148.24	12.82	100.43	Aromatics	[5-8]
176	perfluorodecalin	462.08	20.70	141.29	Fluorocarbons	[9]
177	perfluoromethylcyclohexane	350.05	16.10	107.30	Fluorocarbons	[9]
178	perfluorotoluene	236.06	10.89	79.57	Fluorocarbons	[9]
179	phenol	94.11	6.70	53.88^b	Aromatics	[14]
180	propane	44.10	5.59	37.57	Alkanes	[4-6,29]
181	propionic acid	74.08	6.44	43.64	Carboxylic acids	[4,21]
182	propylbenzene	120.20	10.12	79.97^b	Aromatics	[5-8]
183	propylene	42.08	5.06	30.62^b	Alkenes	[5-8]
184	p-xylene	106.16	8.84	70.66	Aromatics	[4-8]
185	pyridine	79.10	5.60	45.50^b	Amines	[20]
186	s-trioxane	90.08	5.85	41.79^b	^{c}	[20]
187	sulfuryl chloride	134.97	7.50	54.34	Chlorides	[20]
188	terephthalic acid	166.13	10.54	82.80^b	Aromatics	[18]

^{b} V_w calculated following Bondi's method. ^{c} Compounds without a well-defined chemical family.

All A_w were calculated using Bondi's method.

Table C.18: Molecular mass (MM), van der Waals surface area (A_w), van der Waals volume (V_w) and chemical family for each compound in the database - part 9 of 9.

Nr	Compound	MM / g·mol^{-1}	$A_w\cdot10^{-9}$ / cm^2·mol^{-1}	V_w / cm^3·mol^{-1}	Chemical Family	References
189	tert-butanol	74.12	7.82	59.51^b	Alcohols	[5,6,9-14]
190	tert-butyl mercaptan	90.18	6.55	58.59^b	Thiols	[7,12,13,22]
191	tetraethylene glycol	194.23	20.80	109.03	Polyols	[1-4]
192	tetrahydrothiophene	88.10	6.70	52.28^b	^{c}	[20]
193	toluene	92.14	7.42	59.51^b	Aromatics	[5-8]
194	trichloromethane	119.38	6.00	43.54^b	Chlorides	[17]
195	triethylamine	101.19	10.64	76.03^b	Amines	[20]
196	triethylene glycol	150.17	14.20	84.86	Polyols	[1-4]
197	water	18.02	3.50	13.96	^{c}	[17,35]

^{b} V_w calculated following Bondi's method. ^{c} Compounds without a well-defined chemical family.

All A_w were calculated using Bondi's method.

Table C.19: Association energy parameter (ε), association volume (β) and association scheme for each associating compound in the database - part 1 of 3.

Nr	Compound	ε/R_g / K	$\beta\cdot10^3$	Association scheme	References
1	1,2-propylene glycol	2097.9	19.0	4C	[1-4]
5	1-butanol	2525.9	8.2	2B	[4-6,9-14]
6	1-decanol	3013.5	0.0	3B	[15]
8	1-dodecanol	4064.3	0.1	2B	[4-6,9-14]
9	1-heptanol	3160.0	0.3	2B	[4-6,9-14]
10	1-hexanol	2525.9	3.3	2B	[5.6,9-14]
13	1-octanol	3218.5	0.1	2B	[4-6,9-14]
15	1-pentanol	2525.9	3.6	2B	[4-6,9-14]
16	1-propanol	2525.9	8.1	2B	[4-6,9-14]

Table C.20: Association energy parameter (ε), association volume (β) and association scheme for each associating compound in the database - part 2 of 3.

Nr	Compound	ε/R_g / K	$\beta\cdot10^3$	Association scheme	References
19	2-butanol	2526.0	2.2	2B	[4,17]
24	2-methyl-1-propanol	2749.8	1.0	2B	[4-6,9-14]
31	2-octanol	2480.9	1.1	2B	[18]
34	2-propanol	2525.9	9.1	2B	[5,6,9-14,17]
39	acetone	1343.9	289.0	1A	[7,12,13,22]
42	benzoic acid	2049.9	1.2	2B	[7,12,13,22]
43	benzyl alcohol	2470.5	2.4	2B	[5,6,9-14]
47	butylamine	1414.6	33.8	2B	[20]
53	diethanolamine	1943.5	33.2	4C	[17]
55	diethylamine	445.1	110.8	2B	[4,11]
56	diethylene glycol	2367.6	6.4	4C	[1-4]
65	ethanol	2589.8	8.0	2B	[4-6,9-14]
74	ethyl methanoate	5041.7	15.5	1A	[4,21]
79	ethylamine	1120.7	43.0	2B	[4,11]
82	glycerol	1688.1	25	4C	[30]
86	hydrogen sulfide	654.3	58.3	3B	[24]
89	isobutanal	1319.4	0.5	2B	[20]
91	isobutanol	2749.7	1.0	2B	[17]
92	m-cresol	2406.5	6.7	2B	[14]
94	methanol	2957.8	16.1	2B	[4-6,9-14]
99	methyl diethanolamine	1943.5	33.2	4C	[4-6,9-14]
118	methylamine	1379.1	33.7	2B	[4,11]
120	monoethanolamine	1970.0	13.0	4C	[33]
121	monoethylene glycol	2375.8	14.1	4C	[1-4]
124	n-butyl acetate	1136.0	5.9	2B	[4,14,27]
170	o-cresol	1966.3	26.7	2B	[14]

Table C.21: Association energy parameter (ε), association volume (β) and association scheme for each associating compound in the database - part 3 of 3.

Nr	Compound	ε/R_g / K	$\beta\cdot10^3$	Association scheme	References
174	p-cresol	2490.1	4.1	2B	[14]
179	phenol	2103.4	45.3	2B	[14]
181	propionic acid	4808.2	2.1	1A	[4,21]
185	pyridine	1604.1	0.7	2B	[20]
188	terephthalic acid	2049.9	1.2	2x2B	[18]
189	tert-butanol	2572.2	1.0	2B	[5,6,9-14]
191	tetraethylene glycol	1140.8	34.3	4C	[1-4]
192	tetrahydrothiophene	1471.4	46.5	2B	[20]
195	triethylamine	1581.5	77.2	2B	[20]
196	triethylene glycol	1697.1	19.8	4C	[1-4]
197	water	2003.2	69.2	4C	[17,35]

Table C.22: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 1 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
1	1,2-propylene glycol	626.00	5.900	[45]
2	1,3-butadiene	425.17	4.320	[54]
3	1,8-H-perfluorooctane	452.04	d	[4]
4	1-Br-perfluorooctane	541.70	d	[103]
5	1-butanol	563.05	4.414	[43]
6	1-decanol	687.00	2.315	[43]
7	1-decene	616.40	2.220	[54]
8	1-dodecanol	719.40	1.994	[43]
9	1-heptanol	631.90	3.058	[43]
10	1-hexanol	611.35	3.417	[43]

[d] Value not found.

Table C.23: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 2 of 8.

Nr	**Compound**	**T_c / K**	**P_c / MPa**	**References**
11	1-hexene	504.03	3.210	[54]
12	1-H-perfluorooctane	495.94	[d]	[4]
13	1-octanol	652.50	2.777	[43]
14	1-octene	566.60	2.680	[54]
15	1-pentanol	586.15	3.897	[43]
16	1-propanol	536.78	5.169	[43]
17	2,2,4-trimethylpentane	543.96	2.570	[46]
18	2,4-dimethylhexane	553.50	2.560	[46]
19	2-butanol	536.05	4.202	[43]
20	2-butanone	535.50	4.207	[45]
21	2-butenal	565.00	5.497	[44]
22	2-heptanone	611.40	2.970	[45]
23	2-hexanone	587.61	3.300	[45]
24	2-methyl-1-propanol	547.78	4.295	[43]
25	2-methylheptane	559.64	2.500	[46]
26	2-methylhexane	530.37	2.740	[46]
27	2-methylpentane	497.70	3.040	[46]
28	2-methylpropane	408.14	3.640	[46]
29	2-methylpropene	417.90	4.000	[54]
30	2-methylpyridine	622.00	4.600	[55]
31	2-octanol	629.80	2.754	[43]
32	2-octanone	632.70	2.704	[95]
33	2-pentanone	561.05	3.729	[45]
34	2-propanol	508.30	4.764	[43]
35	3-methylpentane	504.43	3.120	[46]
36	4-methyloctane	590.15	2.324	[47]
37	acetic acid	591.95	5.780	[51]

[d] Value not found.

Table C.24: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 3 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
38	acetic anhydride	606.00	4.000	[64]
39	acetone	508.20	4.700	[45]
40	benzaldehyde	695.00	4.410	[51]
41	benzene	562.16	4.895	[65]
42	benzoic acid	751.00	4.560	[66]
43	benzyl alcohol	720.15	4.300	[67]
44	bis(chloromethyl)ether	579.00	4.439	[94]
45	bromine	584.15	10.340	[36]
46	butanal	537.20	4.320	[45]
47	butylamine	524.00	4.154	[56]
48	butylbenzene	660.55	2.890	[65]
49	carbon dioxide	304.21	7.375	[37]
50	carbonyl sulfide	378.80	7.900	[99]
51	cyanogenchloride	566.73	5.282	[77]
52	cyclohexane	536.05	4.080	[46]
53	diethanolamine	736.60	4.620	[57]
54	diethyl ether	466.70	3.644	[45]
55	diethylamine	496.60	3.750	[58]
56	diethylene glycol	744.60	4.661	[96]
57	diisopropyl ether	500.05	2.832	[45]
58	dimethyl carbonate	557.00	4.800	[45]
59	dimethyl disulfide	615.02	5.070	[51]
60	dimethyl ether	400.10	5.340	[45]
61	dimethyl sulfide	503.04	5.530	[100]
62	di-n-propyl-ether	530.60	3.028	[45]
63	dipropyl ether	530.60	3.028	[45]
64	ethane	305.32	4.872	[48]

Table C.25: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 4 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
65	ethanol	513.92	6.137	[43]
66	ethyl benzene	617.20	3.609	[65]
67	ethyl butyrate	571.00	3.100	[45]
68	ethyl decanoate	649.60	1.852	[79]
69	ethyl dodecanoate	705.90	1.580	[80]
70	ethyl ethanoate	523.30	3.870	[45]
71	ethyl hexadecanoate	795.50	1.189	[81]
72	ethyl isopentanoate	587.90	2.967	[82]
73	ethyl mercaptan	499.15	5.490	[100]
74	ethyl methanoate	588.00	4.740	[45]
75	ethyl octanoate	593.80	2.160	[51]
76	ethyl propanoate	546.00	3.450	[45]
77	ethyl propyl ether	500.23	3.370	[45]
78	ethyl tetradecanoate	763.40	1.634	[93]
79	ethylamine	456.15	5.600	[59]
80	ethylbenzene	617.20	3.609	[65]
81	ethylcyclohexane	609.15	3.130	[46]
82	glycerol	766.10	7.500	[45]
83	hexafluorobenzene	517.00	3.280	[103]
84	hexylbenzene	698.00	2.405	[68]
85	hydrogen bromide	363.15	8.561	[75]
86	hydrogen sulfide	373.53	9.010	[101]
87	i-butyl acetate	561.80	3.140	[45]
88	indole	516.85	4.300	[4]
89	isobutanal	513.00	5.100	[45]
90	isobutane	408.14	3.640	[46]
91	isobutanol	547.78	4.295	[43]

Table C.26: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 5 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
92	m-cresol	705.85	4.400	[69]
93	methane	190.56	4.599	[48]
94	methanol	512.64	8.084	[43]
95	methyl bromide	467.00	8.451	[76]
96	methyl butyl ether	512.74	3.370	[45]
97	methyl butyrate	554.50	3.470	[45]
98	methyl decanoate	686.90	1.930	[51]
99	methyl diethanolamine	741.90	4.351	[60}
100	methyl dodecanoate	712.00	1.520	[51]
101	methyl ethanoate	506.55	4.750	[45]
102	methyl heptanoate	612.30	2.360	[51]
103	methyl hexadecanoate	762.20	1.170	[51]
104	methyl hexanoate	590.50	2.530	[51]
105	methyl mercaptan	469.95	7.230	[100]
106	methyl methacrylate	566.00	3.870	[51]
107	methyl methanoate	487.20	6.000	[45]
108	methyl nonanoate	655.70	2.200	[83]
109	methyl octadecanoate	781.10	1.080	[51]
110	methyl octanoate	634.10	2.160	[51]
111	methyl oleate	764.00	1.154	[84]
112	methyl pentadecanoate	786.50	1.364	[85]
113	methyl pentanoate	566.90	3.200	[45]
114	methyl propanoate	530.60	4.000	[45]
115	methyl tetradecanoate	471.20	1.320	[51]
116	methyl tridecanoate	742.90	1.580	[86]
117	methyl undecanoate	699.30	1.750	[51]
118	methylamine	430.05	7.610	[61]

Table C.27: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 6 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
119	methylcyclohexane	572.19	3.480	[46]
120	monoethanolamine	671.40	8.000	[62]
121	monoethylene glyco	720.00	8.000	[45]
122	m-xylene	617.05	3.541	[65]
123	n-butane	425.18	3.796	[48]
124	n-butyl acetate	563.80	3.140	[45]
125	n-butyl butyrate	616.00	2.657	[87]
126	n-butyl ethanoate	563.80	3.140	[45]
127	n-butyl mercaptan	570.10	4.000	[100]
128	n-butyl methanoate	559.00	3.713	[88]
129	n-butyl nonanoate	674.00	1.708	[89]
130	n-butyl octadecanoate	764.00	0.927	[90]
131	n-butyl pentanoate	629.00	2.412	[91]
132	n-butyl propanoate	594.60	2.941	[92]
133	n-decane	617.70	2.110	[48]
134	n-docosane	787.00	0.980	[48]
135	n-dodecane	658.00	1.820	[48]
136	n-dotriacontane	855.00	0.543	[49]
137	n-eicosane	768.00	1.070	[48]
138	n-heneicosane	778.00	1.030	[48]
139	n-heptacosane	826.00	0.688	[50}
140	n-heptane	540.20	2.740	[48]
141	n-hexacosane	819.00	0.810	[51]
142	n-hexadecane	723.00	1.400	[48]
143	n-hexane	507.60	3.025	[48]
144	n-hexatriacontane	874.00	0.580	[51]
145	nitrobenzene	720.00	4.825	[70]

Table C.28: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 7 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
146	nitrogen	126.20	3.394	[38]
147	n-nonacosane	838.00	0.624	[52]
148	n-nonadecane	758.00	1.160	[48]
149	n-nonane	594.60	2.290	[48]
150	n-octacosane	832.00	0.750	[51]
151	n-octadecane	747.00	1.290	[48]
152	n-octane	568.70	2.490	[48]
153	n-pentacosane	812.00	0.764	[53]
154	n-pentadecane	708.00	1.480	[48]
155	n-pentane	469.70	3.370	[48]
156	n-perfluoroheptane	475.30	1.630	[103]
157	n-perfluorohexane	449.00	1.850	[103]
158	n-perfluorononane	523.95	1.560	[103]
159	n-perfluorooctane	498.00	1.500	[103]
160	n-propyl butyrate	593.70	2.720	[45]
161	n-propyl ethanoate	549.70	3.360	[45]
162	n-propyl mercaptan	536.60	4.600	[100]
163	n-propyl methanoate	538.00	4.060	[45]
164	n-propyl propanoate	568.60	3.060	[45]
165	n-tetracosane	804.00	0.870	[48]
166	n-tetradecane	693.00	1.570	[48]
167	n-triacontane	844.00	0.690	[51]
168	n-tricosane	796.00	0.920	[48]
169	n-undecane	639.00	1.980	[48]
170	o-cresol	697.55	4.200	[71]
171	octafluorotoluene	534.47	2.680	[103]
172	oxygen	154.58	5.080	[39]

Table C.29: Critical temperature (T_c) and critical pressure (P_c) for all the compounds in the database - part 8 of 8.

Nr	Compound	T_c / K	P_c / MPa	References
173	o-xylene	630.30	3.732	[65]
174	p-cresol	704.65	4.100	[72]
175	pentylbenzene	679.90	2.648	[73]
176	perfluorodecalin	566.00	1.780	[103]
177	perfluoromethylcyclohexane	485.90	2.019	[103]
178	perfluorotoluene	534.50	2.705	[103]
179	phenol	694.25	5.930	[45]
180	propane	369.83	4.248	[48]
181	propionic acid	600.81	4.670	[51]
182	propylbenzene	638.38	3.200	[65]
183	propylene	364.90	4.600	[54]
184	p-xylene	616.23	3.511	[65]
185	pyridine	619.00	5.650	[57]
186	s-trioxane	585.00	5.962	[40]
187	sulfuryl chloride	542.15	4.610	[4]
188	terephthalic acid	883.60	5.407	[74]
189	tert-butanol	506.20	3.972	[43]
190	tert-butyl mercaptan	530.01	4.334	[102]
191	tetraethylene glycol	795.00	3.200	[97]
192	tetrahydrothiophene	632.00	5.138	[41]
193	toluene	591.80	4.108	[65]
194	trichloromethan	536.40	5.328	[78]
195	triethylamine	535.35	3.100	[63]
196	triethylene glycol	769.50	3.300	[98]
197	water	647.29	22.089	[42]

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Appendix D

Studies of dependence in pure compounds

In this appendix, all the studies of dependence between pure compound parameters which were not presented in the main text shall be found.

Later, some important comparisons will be made. Firstly, the pure compounds' database of this project, present in Appendix C, will be compared with the one earlier assembled by Schlaikjer [1]. Afterwards, the performance of the energy term parameter a_0 will be compared with the one of the corrected energy parameter, Γ. Lastly, the determination coefficients of the fits involving the van der Waals volume, V_w, will be compared with the ones of the van der Waals surface area, A_w.

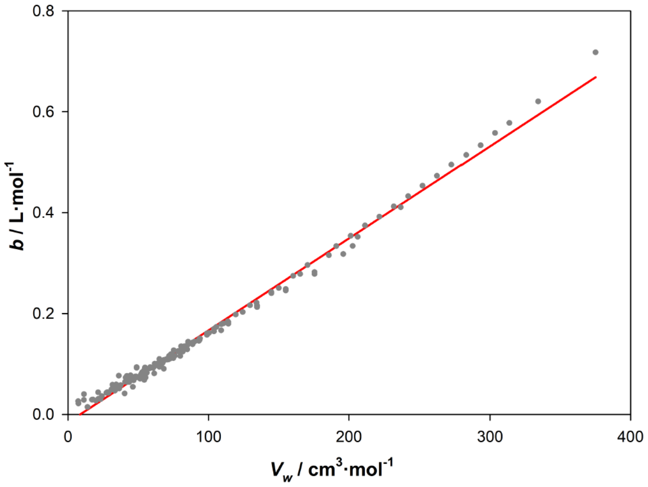

Fig. D.1: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w. The regression (–) follows equation $b = 1.82 \cdot 10^{-3} \cdot V_\mathrm{w} - 0.02$, with a determination coefficient of 0.9928.

D.1 Plots considering fluorocarbons

In this section, the studies of dependence of the energy term parameter, a_0, and of the co-volume parameter, b, with the van der Waals volume, as well as a_0 with b are presented, including the chemical compounds earlier classified as fluorocarbons in Tables C.10 to C.16 in Appendix C.

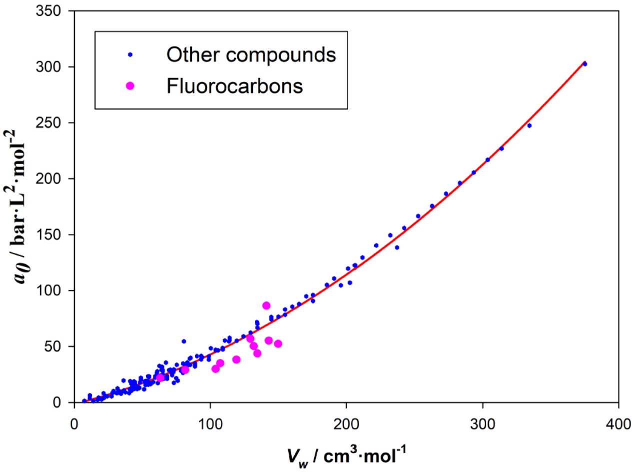

Fig. D.2: Study of dependence of the term energy parameter, a_0, with the van der Waals volume, V_w, including the fluorocarbons family. The regression (–) follows equation $a_0 = 1.36 \cdot 10^{-3} \cdot V_w^2 + 0.31 \cdot V_w - 1.45$, with a determination coefficient of 0.9888.

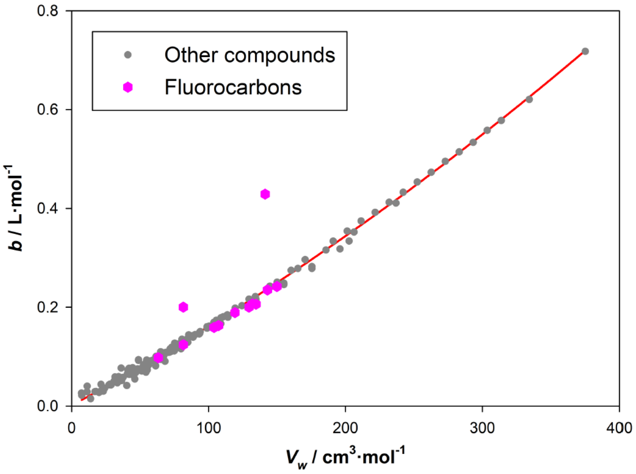

Fig. D.3: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, including the fluorocarbons family. The regression (–) follows equation $b = 1.15 \cdot 10^{-6} \cdot V_w^2 + 1.48 \cdot 10^{-3} \cdot V_{+}1.35 \cdot 10^{-3}$, with a determination coefficient of 0.9824.

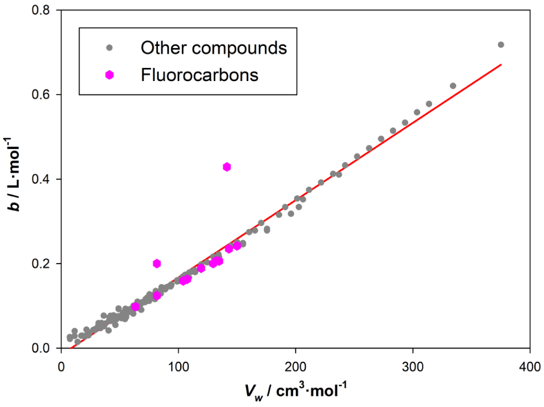

Fig. D.4: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_{w}, including the fluorocarbons family. The regression (–) follows equation $b = 1.83 \cdot 10^{-3} \cdot V_{\mathrm{w}} - 0.02$, with a determination coefficient of 0.9789.

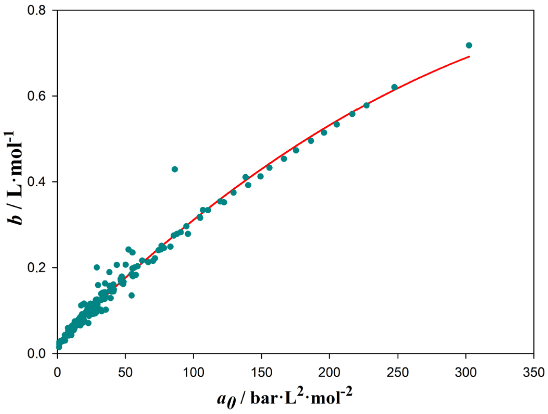

Fig. D.5: Study of dependence of the co-volume parameter, b, with the energy term parameter, a_0, including the fluorocarbons family. The regression (–) follows equation $b = -3.20 \cdot 10^{-6} \cdot a_0^2 + 3.17 \cdot 10^{-3} \cdot a_0 - 0.03$, with a determination coefficient of 0.9780.

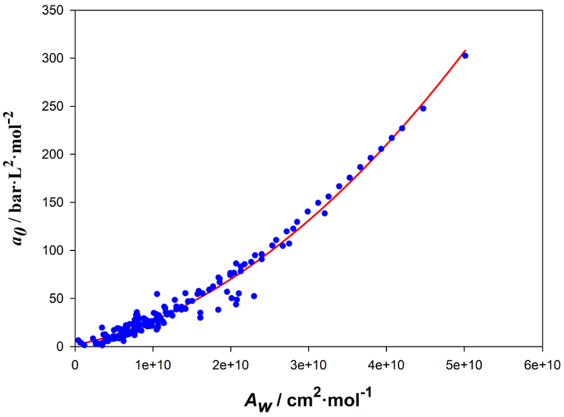

Fig. D.6: Study of dependence of the energy term parameter, a_0, with the van der Waals surface area, A_{w}, including the fluorocarbons family. The regression (–) follows equation $a_0 = 8.92 \cdot 10^{-20} \cdot A_{\mathrm{w}}^2 + 1.64 \cdot 10^{-9} \cdot A_{\mathrm{w}} + 1.59$, with a determination coefficient of 0.9777.

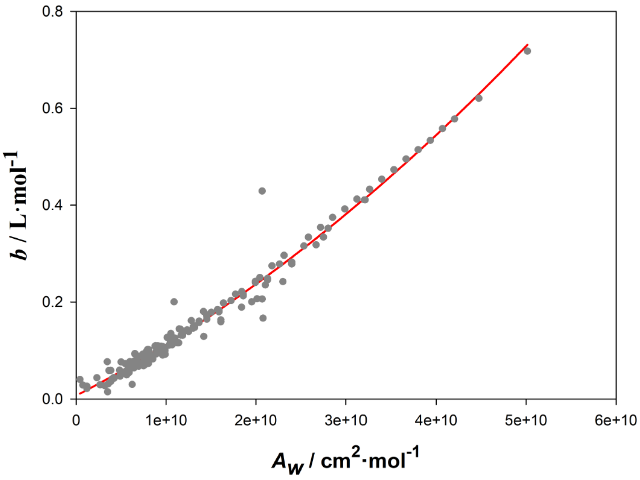

Fig. D.7: Study of dependence of the co-volume, b, with the van der Waals surface area, A_w, including the fluorocarbons family. The regression (–) follows equation $b = 9.78 \cdot 10^{-23} \cdot A_\text{w}^2 + 9.54 \cdot 10^{-12} \cdot A_\text{w} + 7.07 \cdot 10^{-3}$, with a determination coefficient of 0.9756.

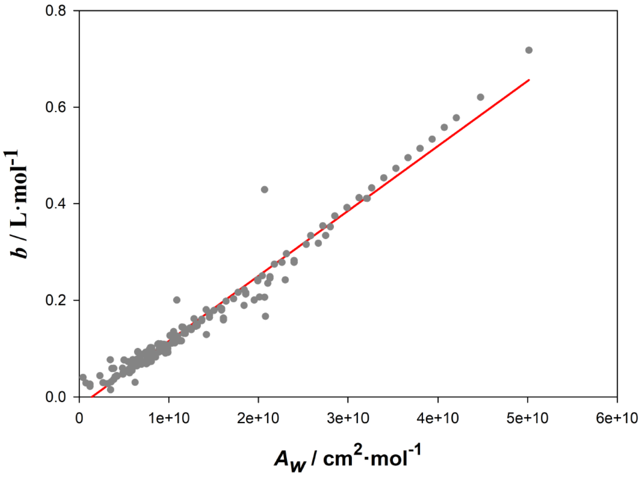

Fig. D.8: Study of dependence of the co-volume, b, with the van der Waals surface area, A_w, including the fluorocarbons family. The regression (–) follows equation $b = 1.35 \cdot 10^{-11} \cdot A_\text{w} - 0.02$, with a determination coefficient of 0.9673.

D.2 Additional plots

In this section, additional plots are shown, some comprising extra fitting equations and others studying only compounds with molecular mass below 240 g·mol^{-1}.

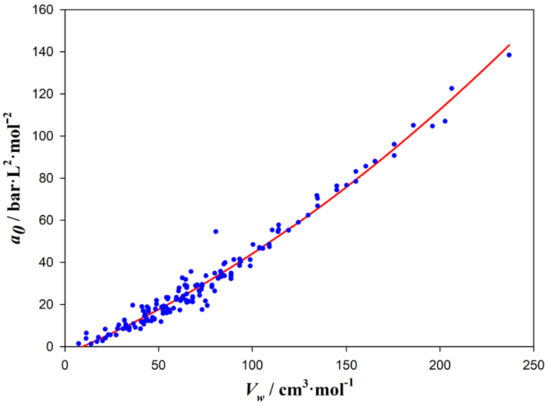

Fig. D.9: Study of dependence of the term energy parameter, a_0, with the van der Waals volume, V_w, without high molecular mass alkanes. The regression (–) follows equation $a_0 = 1.04 \cdot 10^{-3} \cdot V_\text{w}^2 + 0.37 \cdot V_\text{w} - 3.62$, with a determination coefficient of 0.9758.

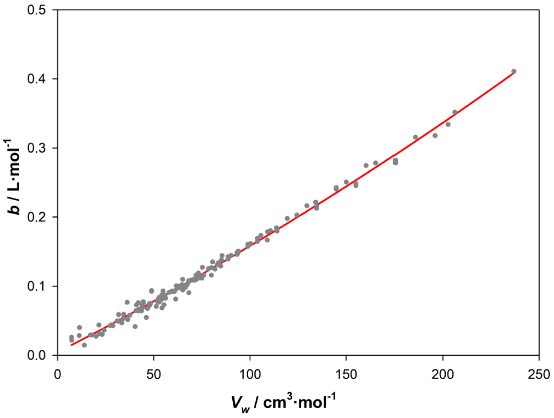

Fig. D.10: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, without high molecular mass alkanes. The regression (–) follows equation $b = 1.23 \cdot 10^{-6} \cdot V_\text{w}^2 + 1.41 \cdot 10^{-3} \cdot V_\text{w} + 4.49 \cdot 10^{-3}$, with a determination coefficient of 0.9918.

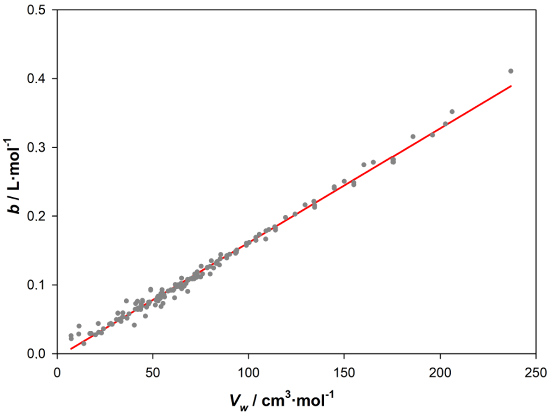

Fig. D.11: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, without high molecular mass alkanes. The regression (–) follows equation $b = 1.66 \cdot 10^{-3} \cdot V_\text{w} - 4.99 \cdot 10^{-3}$, with a determination coefficient of 0.9897.

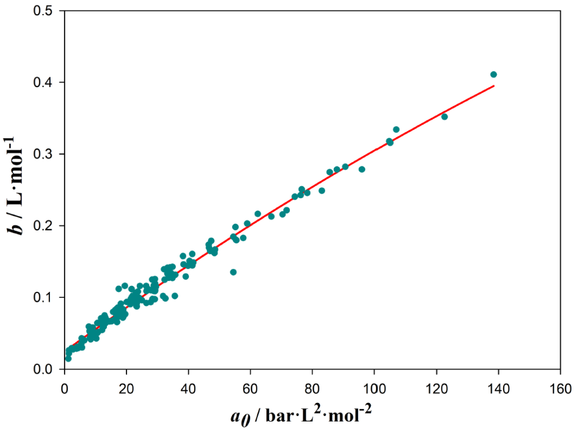

Fig. D.12: Study of dependence of the co-volume parameter, b, with the energy term parameter, a_0, without high molecular mass alkanes. The regression (–) follows equation $b = -3.27\cdot10^{-6}\cdot a_0^2 + 3.13\cdot10^{-3}\cdot a_0 + 0.02$, with a determination coefficient of 0.9789.

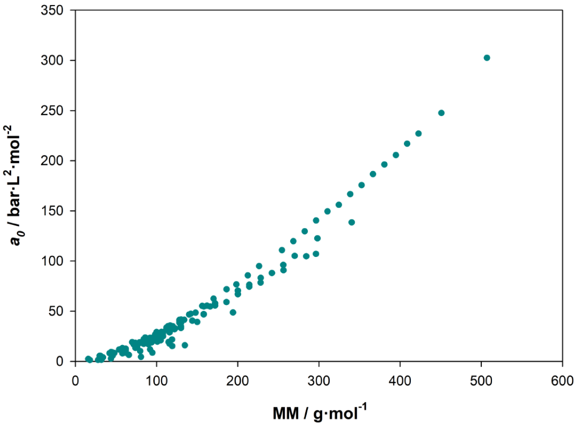

Fig. D.13: Study of dependence of the energy term parameter, a_0, with the molecular mass, MM.

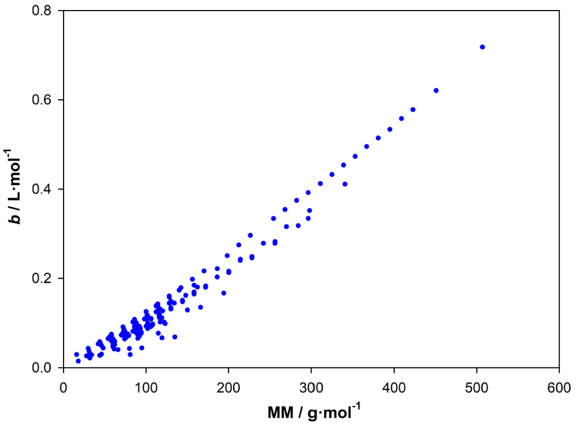

Fig. D.14: Study of dependence of the co-volume, b, with the molecular mass, MM.

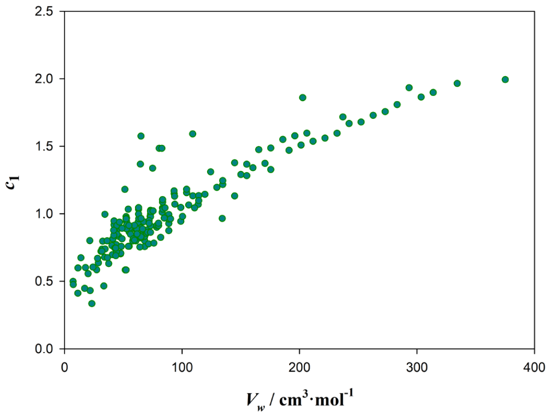

Fig. D.15: Study of dependence of the energy term parameter, c_1, with the van der Waals volume, V_w.

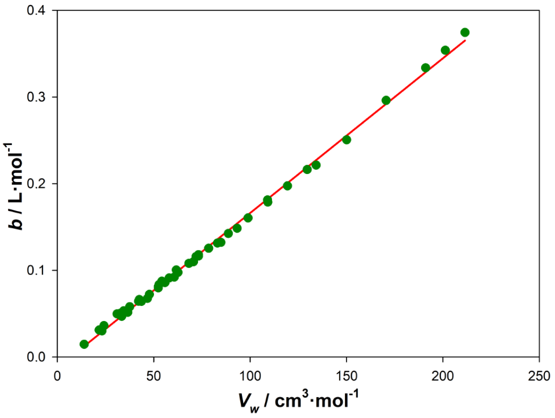

Fig. D.16: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, for Schlaikjer's database [1]. The regression (–) follows equation $b = 1.79 \cdot 10^{-3} \cdot V_w - 0.01$, with a determination coefficient of 0.9981.

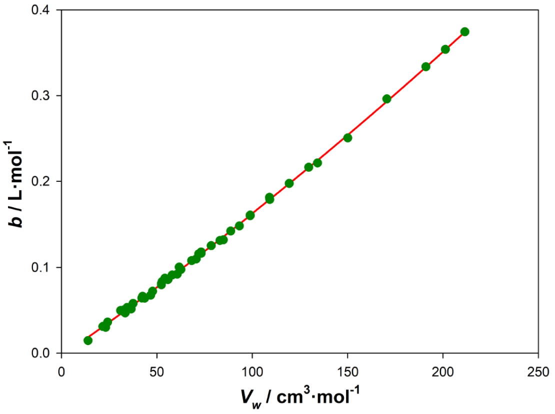

Fig. D.17: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, for Schlaikjer's database [1]. The regression (–) follows equation $b = 1.15 \cdot 10^{-6} \cdot V_w^2 + 1.54 \cdot 10^{-3} \cdot V_w - 3.27 \cdot 10^{-3}$, with a determination coefficient of 0.9994.

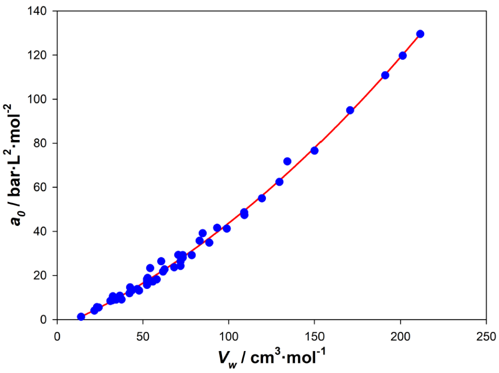

Fig. D.18: Study of dependence of the energy term parameter, a_0, with the van der Waals volume, V_w, for Schlaikjer's database [1]. The regression (–) follows equation $a_0 = 1.40 \cdot 10^{-3} \cdot V_w^2 + 0.33 \cdot V_w - 3.61$, with a determination coefficient of 0.9959.

D.3 Alkanes

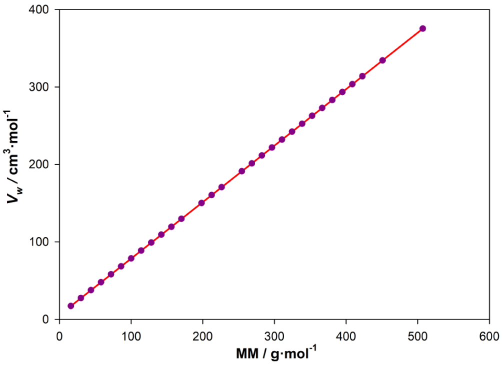

Fig. D.19: Study of dependence of the van der Waals volume, V_w, with the molecular mass, MM, in alkanes. The regression (–) follows equation $V_w = 0.73 \cdot \text{MM} + 5.41$, with a determination coefficient of 1.0000.

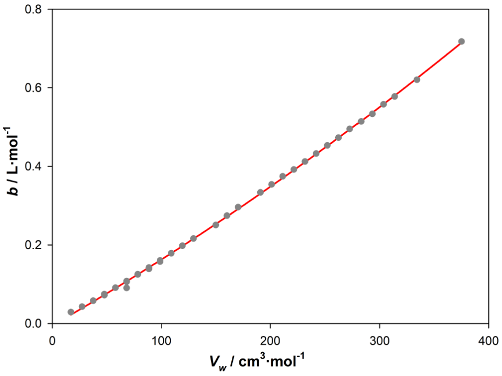

Fig. D.20: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w in alkanes. The regression (–) follows equation $b = 8.76 \cdot 10^{-7} \cdot V_w^2 + 1.59 \cdot 10^{-3} \cdot V_w - 5.14 \cdot 10^{-3}$, with a determination coefficient of 0.9996.

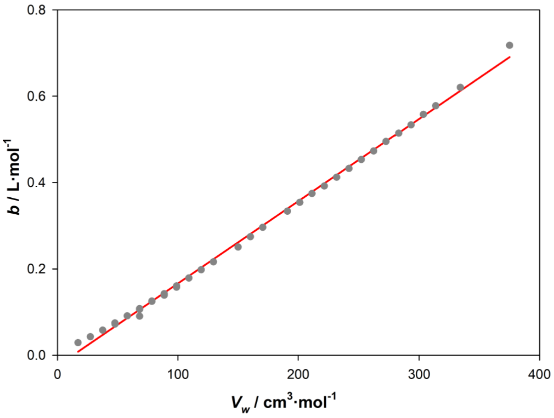

Fig. D.21: Study of dependence of the co-volume parameter, b, with the van der Waals volume, V_w, in alkanes. The regression (–) follows equation $b = 1.91 \cdot 10^{-3} \cdot V_w - 0.02$, with a determination coefficient of 0.9981.

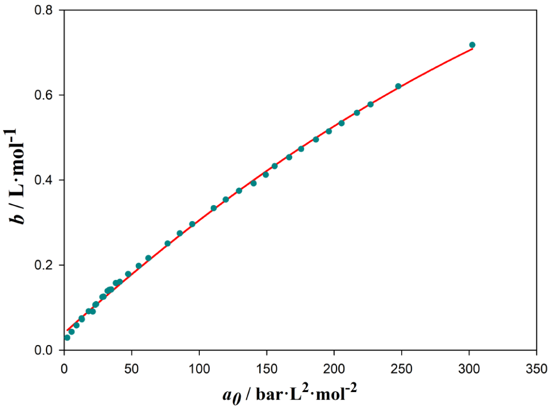

Fig. D.22: Study of dependence of the co-volume parameter, b, with the energy term parameter, a_0, in alkanes. The regression (–) follows equation $b = -2.18 \cdot 10^{-6} \cdot a_0^2 + 2.87 \cdot 10^{-3} \cdot a_0 - 0.04$, with a determination coefficient of 0.9989.

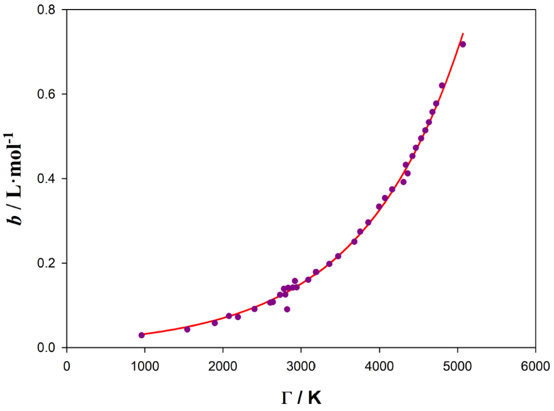

Fig. D.23: Study of dependence of the co-volume parameter, b, with the corrected energy term parameter, Γ, in alkanes. The regression (–) follows equation $b = -1.40 \cdot 10^{-2} + 1.83 \cdot 10^{-2} \cdot e^{0.00733 \cdot \Gamma}$, with a determination coefficient of 0.9968.

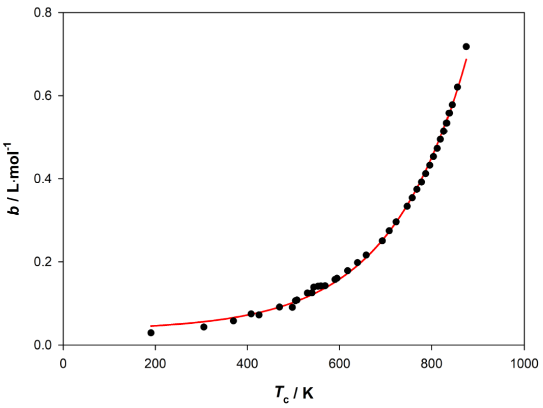

Fig. D.24: Study of dependence of the co-volume parameter, b, with the critical temperature, T_c, in alkanes. The regression (–) follows equation $b = 3.56 \cdot 10^{-2} + 3.19 \cdot 10^{-3} \cdot e^{0.00609 \cdot T_c}$, with a determination coefficient of 0.9978.

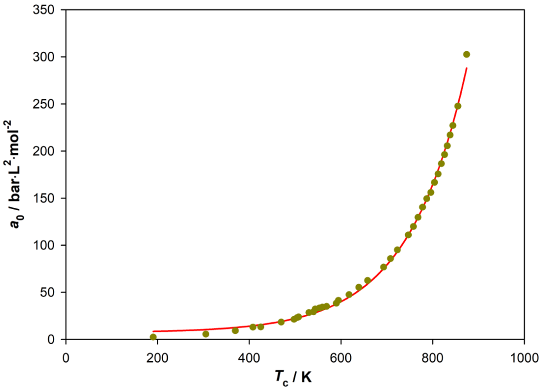

Fig. D.25: Study of dependence of the energy term parameter, a_0, with the critical temperature, T_c, in alkanes. The regression (–) follows equation $a_0 = 7.13 + 2.99 \cdot 10^{-1} \cdot e^{0.00783 \cdot T_c}$, with a determination coefficient of 0.9981.

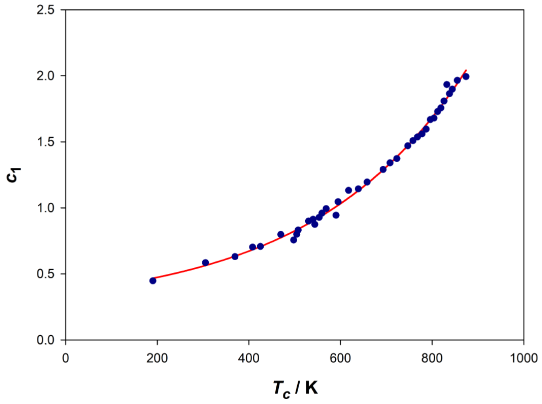

Fig. D.26: Study of dependence of the energy term parameter, c_1, with the critical temperature, T_c, in alkanes. The regression (–) follows equation $c_1 = 0.228 + 0.136 \cdot e^{0.00297 \cdot T_c}$, with a determination coefficient of 0.9954.

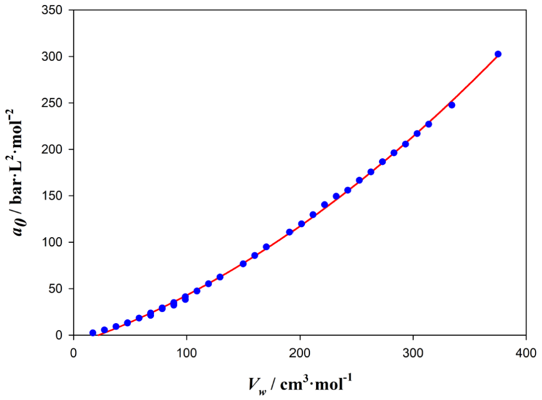

Fig. D.27: Study of dependence of the energy term parameter, a_0, with the van der Waals volume, V_w, in alkanes. The regression (–) follows equation $a_0 = 1.10 \cdot 10^{-3} \cdot V_\text{w}^2 + 0.42 \cdot V_\text{w} - 9.73$, with a determination coefficient of 0.9994.

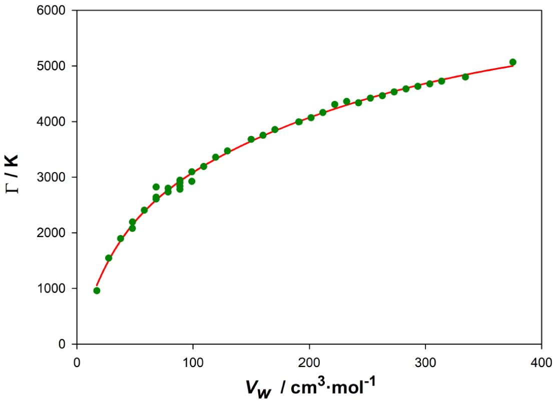

Fig. D.28: Study of dependence of the corrected energy term parameter, Γ, with the van der Waals volume, V_w, in alkanes. The regression (–) follows equation $\Gamma = 4.14 \cdot 10^3 \cdot (1 - e^{-0.0427 \cdot V_\text{w}}) + 1.70 \cdot 10^3 \cdot (1 - e^{-0.00350 \cdot V_\text{w}})$, with a determination coefficient of 0.9963.

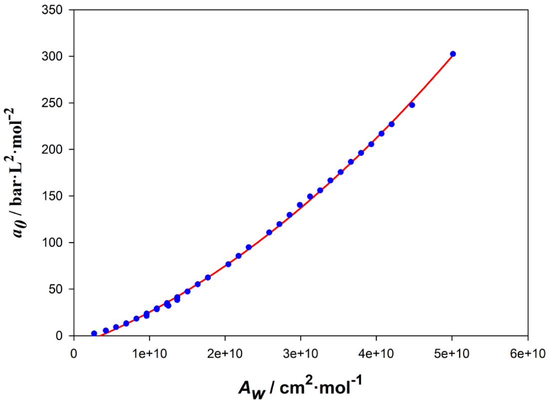

Fig. D.29: Study of dependence of the energy term parameter, a_0, with the van der Waals surface area, A_w, in alkanes. The regression (–) follows equation $a_0 = 6.36 \cdot 10^{-20} \cdot A_\text{w}^2 + 3.05 \cdot 10^{-9} \cdot A_\text{w} - 11.52$, with a determination coefficient of 0.9993.

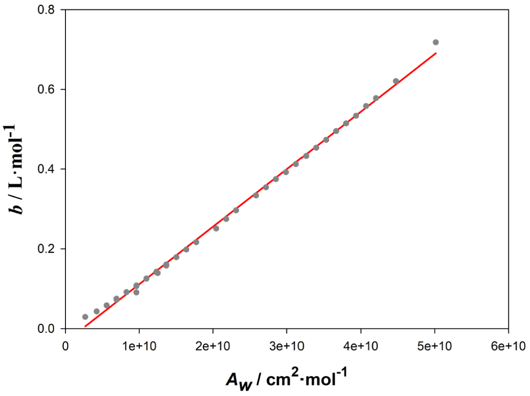

Fig. D.30: Study of dependence of the co-volume, b, with the van der Waals surface area, A_w, in alkanes. The regression (–) follows equation $b = 1.44 \cdot 10^{-11} \cdot A_\mathrm{w} - 0.03$, with a determination coefficient of 0.9980.

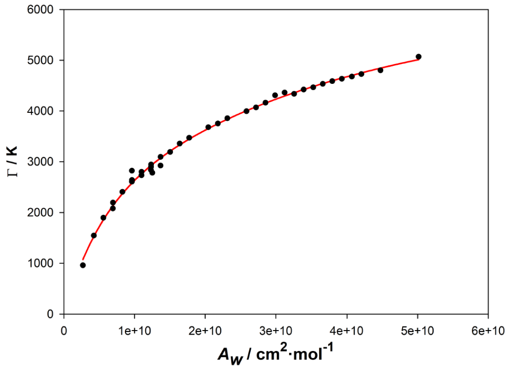

Fig. D.31: Study of dependence of the corrected energy term parameter, Γ, with the van der Waals surface area, A_w, in alkanes. The regression (–) follows equation $\Gamma = 4.16 \cdot 10^3 \cdot (1 - e^{-2.77 \cdot 10^{-11} \cdot A_\mathrm{w}}) + 1.89 \cdot 10^3 \cdot (1 - e^{-1.97 \cdot 10^{-10} \cdot A_\mathrm{w}})$, with a determination coefficient of 0.9957.

D.4 Association energy and cross-association volume

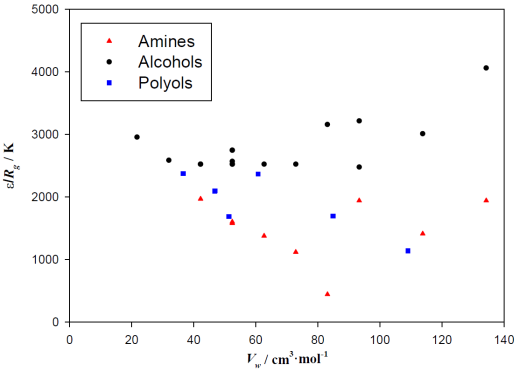

Fig. D.32: Study of dependence of the association energy parameter, ε, with the van der Waals volume, V_w, for alcohols, amines and polyols.

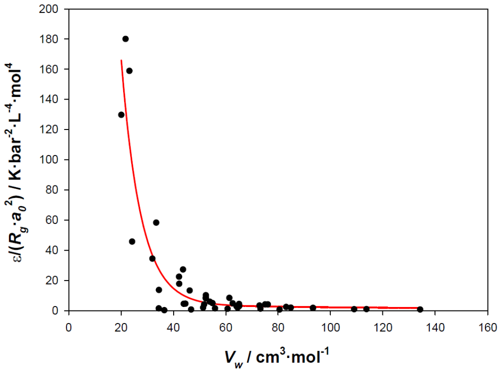

Fig. D.33: Study of dependence of a function of the association energy parameter, ε, and of the energy term parameter, a_0, with the van der Waals volume, V_w, for all the associating compounds except hydrogen sulfide and water. The regression (–) follows equation $\frac{\varepsilon}{R_g \cdot a_0^2} = 4.59 \cdot e^{-0.007 \cdot V_\mathrm{w}} + 2.37 \cdot 10^3 \cdot e^{-0.13 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.8387.

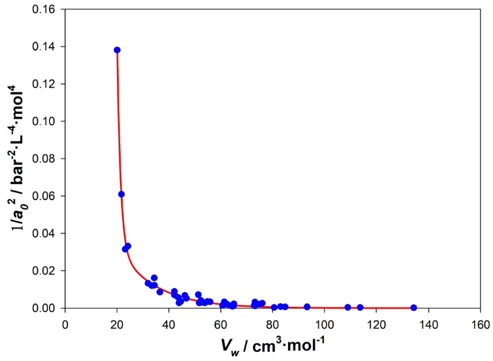

Fig. D.34: Study of dependence of the inverse of the squared energy term parameter, a_0, with the van der Waals volume, V_w, for all the associating compounds except hydrogen sulfide and water. The regression (–) follows equation $\frac{1}{a_0^2} = 4.12 \cdot 10^5 \cdot e^{-0.76 \cdot V_\mathrm{w}} + 1.26 \cdot 10^{-1} e^{-0.068 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.9947.

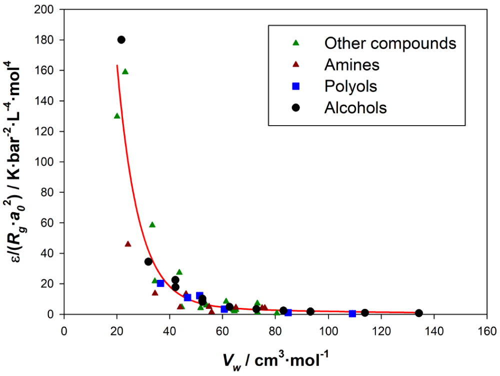

Fig. D.35: Study of dependence of a function of the association energy parameter, ε, and of the energy term parameter, a_0, with the van der Waals volume, V_w, for all the associating compounds except hydrogen sulfide and water, per family. The regression (–) follows equation $\frac{\varepsilon}{R_g \cdot a_0^2} = 8.40 \cdot e^{-0.015 \cdot V_\mathrm{w}} + 1.85 \cdot 10^3 \cdot e^{-0.013 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.8556.

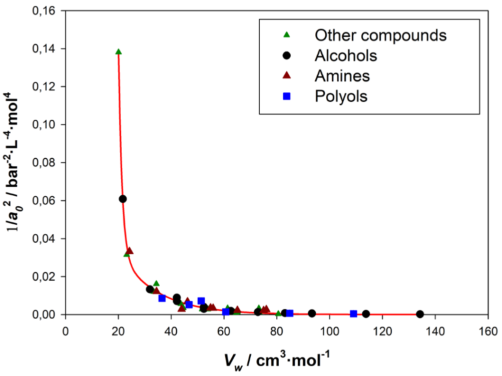

Fig. D.36: Study of dependence of the inverse of the squared energy term parameter, a_0, with the van der Waals volume, V_w, for all the associating compounds except hydrogen sulfide and water, per family. The regression (–) follows equation $\frac{1}{a_0^2} = 4.12 \cdot 10^5 \cdot e^{-0.76 \cdot V_\mathrm{w}} + 1.26 \cdot 10^{-1} e^{-0.068 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.9947.

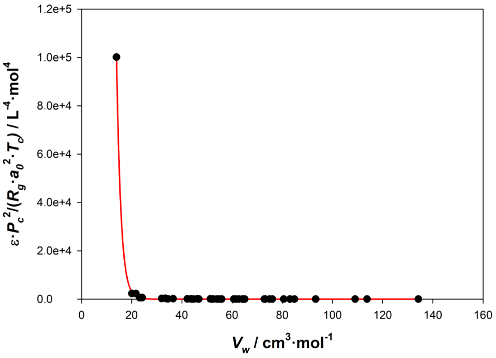

Fig. D.37: Study of dependence of a function of the association energy parameter, of the energy term parameter and of the critical properties, $\varepsilon \cdot P_c^2/(R_g \cdot a_0^2 \cdot T_c)$, with the van der Waals volume for all the associating compounds except hydrogen sulfide. The regression (–) follows equation $\frac{\varepsilon \cdot P_c^2}{R_g \cdot a_0^2 \cdot T_c} = 3.09 \cdot 10^8 \cdot e^{-0.58 \cdot V_\mathrm{w}} + 1.38 \cdot 10^5 \cdot e^{-1.60 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.9998.

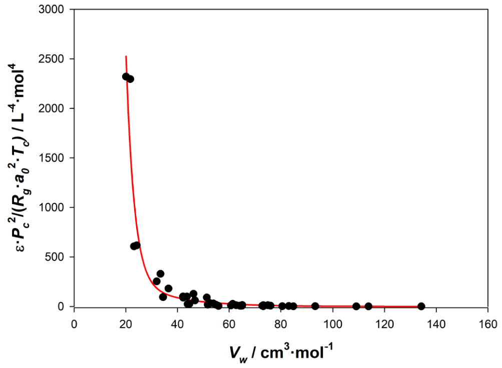

Fig. D.38: Study of dependence of a function of the association energy parameter, of the energy term parameter and of the critical properties, $\varepsilon \cdot P_c^2/(R_g \cdot a_0^2 \cdot T_c)$, with the van der Waals volume for all the associating compounds except hydrogen sulfide and water. The regression (–) follows equation $\frac{\varepsilon \cdot P_c^2}{R_g \cdot a_0^2 \cdot T_c} = 1.38 \cdot 10^6 \cdot e^{-0.32 \cdot V_\mathrm{w}} + 8.52 \cdot 10^2 \cdot e^{-0.058 \cdot V_\mathrm{w}}$, with a determination coefficient of 0.9180.

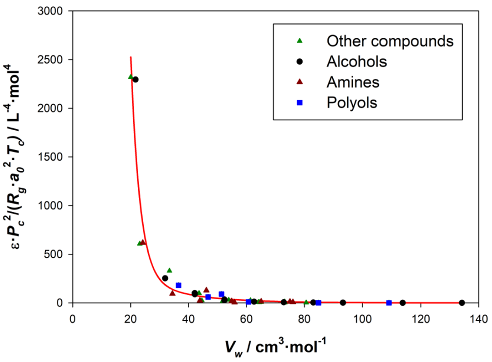

Fig. D.39: Study of dependence of a function of the association energy parameter, of the energy term parameter and of the critical properties, $\varepsilon\cdot P_c^2/(R_g\cdot a_0^2\cdot T_c)$, with the van der Waals volume for all the associating compounds except hydrogen sulfide and water, per family. The regression (–) follows equation $\frac{\varepsilon\cdot P_c^2}{R_g\cdot a_0^2\cdot T_c} = 1.38\cdot 10^6\cdot e^{-0.32\cdot V_\mathrm{w}} + 8.52\cdot 10^2\cdot e^{-0.058\cdot V_\mathrm{w}}$, with a determination coefficient of 0.9180.

D.5 van der Waals surface area

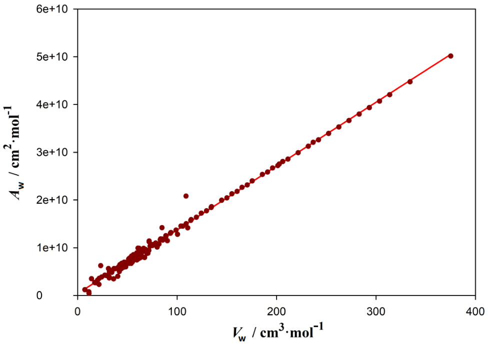

Fig. D.40: Study of dependence of the van der Waals surface area, A_w, with the van der Waals volume, V_w. The regression (–) follows equation $A_\mathrm{w} = 1.34\cdot 10^8\cdot V_\mathrm{w} + 3.92\cdot 10^8$, with a determination coefficient of 0.9934.

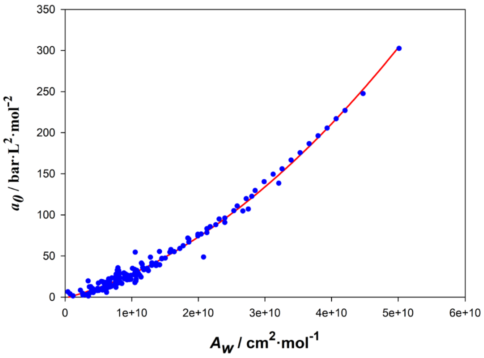

Fig. D.41: Study of dependence of the energy term parameter, a_0, with the van der Waals surface area, A_w. The regression (–) follows equation $a_0 = 7.93\cdot 10^{-20}\cdot A_\mathrm{w}^2 + 2.13\cdot 10^{-9}\cdot A_\mathrm{w} - 1.16$, with a determination coefficient of 0.9883.

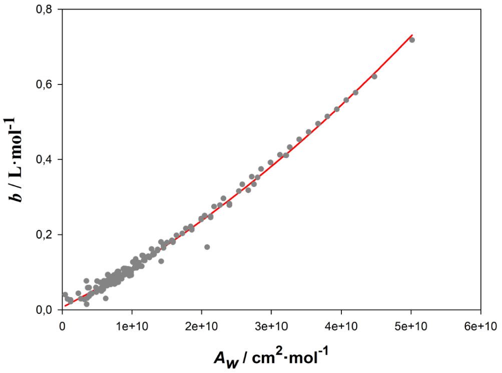

Fig. D.42: Study of dependence of the co-volume, b, with the van der Waals surface area, A_w. The regression (–) follows equation $b = 9.71 \cdot 10^{-23} \cdot A_\mathrm{w}^2 + 9.58 \cdot 10^{-12} \cdot A_\mathrm{w} + 6.44 \cdot 10^{-3}$, with a determination coefficient of 0.9883.

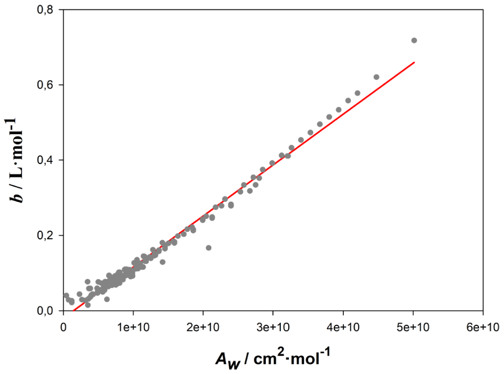

Fig. D.43: Study of dependence of the co-volume, b, with the van der Waals surface area, A_w. The regression (–) follows equation $b = 1.35 \cdot 10^{-11} \cdot A_\mathrm{w} - 0.019$, with a determination coefficient of 0.9831.

D.6 Critical properties

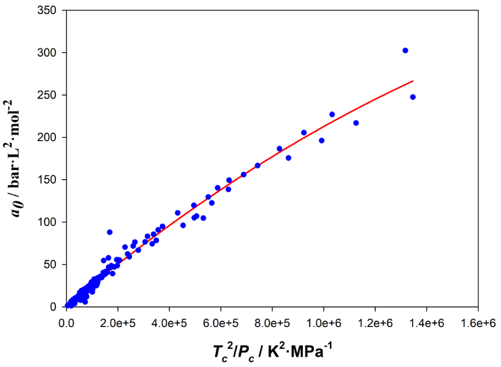

Fig. D.44: Study of dependence of the energy term parameter, a_0, with a function of the critical properties, T_c^2/P_c. The regression (–) follows equation $a_0 = -4.17 \cdot 10^{-11} \cdot (T_c^2/P_c)^2 + 2.53 \cdot 10^{-4} \cdot (T_c^2/P_c) + 1.45$, with a determination coefficient of 0.9819.

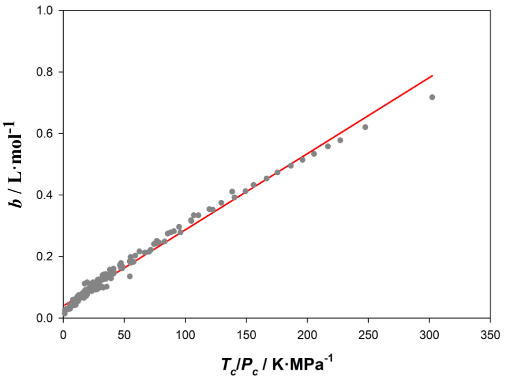

Fig. D.45: Study of dependence of the co-volume, b, with a function of the critical properties, T_c/P_c. The regression (–) follows equation $b = 2.10 \cdot 10^{-4} \cdot T_c/P_c + 5.52$, with a determination coefficient of 0.9768.

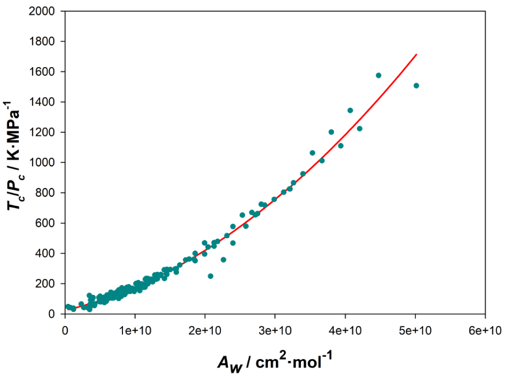

Fig. D.46: Study of dependence of a function of the critical properties, T_c/P_c, with the van der Waals surface area, A_w. The regression (–) follows equation $T_c/P_c = 4.62 \cdot 10^{-19} \cdot A_\mathrm{w}^2 + 1.05 \cdot 10^{-8} \cdot A_\mathrm{w} + 24.24$, with a determination coefficient of 0.9837.

Table D.1: Comparison between the number of compounds per chemical family in this project's database and the database previously assembled by Schlaikjer [1].

Chemical Family	**Project's database**	**Schlaikjer's database**
Alcohols	16	10
Aldehydes	3	-
Alkanes	39	15
Alkenes	6	-
Amines	10	3
Anhydrides	1	1
Aromatics	21	1
Bromides	2	-
Carboxylic acids	2	3
Chlorides	3	-
Cycloalkenes	3	-
Esters	43	5
Ethers	8	4
No well-defined family	7	1
Ketones	6	-
Polyols	6	5
Sulfides	4	-
Thiols	5	-
Total	**185**	**48**

Table D.2: Regression types and determination coefficients for the fits of the energy term parameter (a_0) and of the corrected energy term parameter (Γ) with the co-volume (b), with the van der Waals volume (V_w) and with the molecular mass (MM).

Independent variable	**Dependent variable**	**Chemical family**	**Determination coefficient**	**Regression type**	**Corresponding figure**
a_0	b	All compounds	0.9780	2nd degree	D.5
Γ	b		0.7041	2nd degree	[e]
V_w	a_0		0.9888	2nd degree	D.2
V_w	Γ		0.6536	2nd degree	[e]
a_0	b	All compounds except fluorocarbons	0.9925	2nd degree	4.3
Γ	b		0.7478	2nd degree	[e]
V_w	a_0		0.9941	2nd degree	4.1
V_w	Γ		0.7153	2nd degree	[e]
V_w	a_0	Alkanes	0.9994	2nd degree	D.27
V_w	Γ		0.9963	Equation 4.1	D.28
a_0	b		0.9989	2nd degree	D.22
Γ	b		0.9968	Equation 4.1	D.23
MM	a_0		0.9994	2nd degree	4.5
MM	Γ		0.9963	Equation 4.1	4.6

[e] Figure not present in the document due to a low determination coefficient.

Table D.3: Regression types and determination coefficients for the fits of the van der Waals volume (V_w) and of the van der Waals surface area (A_w) with the energy term parameter (a_0), with the co-volume (b), with the corrected energy term parameter (Γ) and with functions of the energy term parameter and association energy.

Independent variable	Dependent variable	Chemical family	Determination coefficient	Regression type	Corresponding figure
V_w	a_0	All compounds	0.9888	2nd degree	D.2
A_w	a_0		0.9777	2nd degree	D.6
V_w	b		0.9789	1st degree	D.4
A_w	b		0.9673	1st degree	D.8
V_w	a_0	All compounds except fluorocarbons	0.9941	2nd degree	4.1
A_w	a_0		0.9883	2nd degree	D.41
V_w	b		0.9928	1st degree	D.1
A_w	b		0.9831	1st degree	D.43
V_w	a_0	Alkanes	0.9994	2nd degree	D.27
A_w	a_0		0.9993	2nd degree	D.29
V_w	b		0.9981	1st degree	D.21
A_w	b		0.9980	1st degree	D.30
V_w	Γ		0.9963	Equation 4.1	D.28
A_w	Γ		0.9957	Equation 4.1	D.31
V_w	$\varepsilon/(R_g \cdot a_0^2)$	Associating compounds	0.8556	Equation 4.2	D.33
A_w	$\varepsilon/(R_g \cdot a_0^2)$		0.3373	Equation 4.2	[e]
V_w	$1/a_0^2$		0.9947	Equation 4.2	D.34
A_w	$1/a_0^2$		0.4086	Equation 4.2	[e]

[e] Figure not present in the document due to a low determination coefficient.

D.7 Bibliography

[1] A. Schlaikjer. Towards a predictive CPA equation of state for chemical applications. Master's thesis, Technical University of Denmark, Denmark, 2014.

Appendix E

Predicting properties in pure compounds

To predict vapour pressure and liquid density, four different methods were applied, the first one using the Cubic Plus Association equation of state (CPA EoS) and the parameters from appendix C, the second one making usage of the CPA EoS and some correlated parameters, the third using the correlated parameters from the second method and fitting another one to experimental data and the last method using two fitted parameters and a correlated one. All the alternatives were compared to the correlations from the Design Institute for Physical Properties (DIPPR), which were considered experimental data.

In this appendix, some figures comparing this project's results with data from the DIADEM Professional database and comparing some parameters with their correlated versions can be found.

Laslty, from Table E.1 to E.7, the correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods can be observed. Moreover, from Table E.8 to E.23, the average absolute deviations (AAD) between the predicted properties and their experimental references are presented per chemical compound. On the other hand, they are sorted by chemical family in Tables E.24 and E.25.

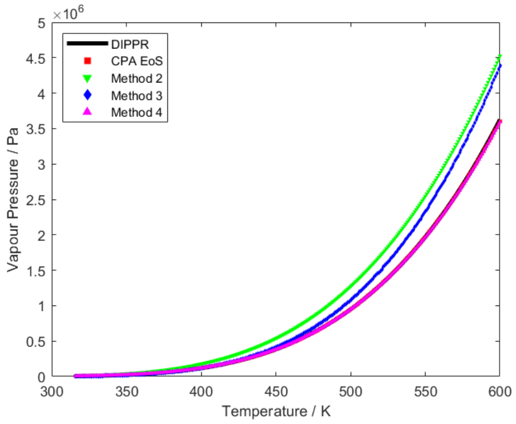

Fig. E.1: Vapour pressures predicted from the CPA EoS and from the three other methods for tetrahydrothiophene, with an ADD of 0.1 % in the CPA EoS.

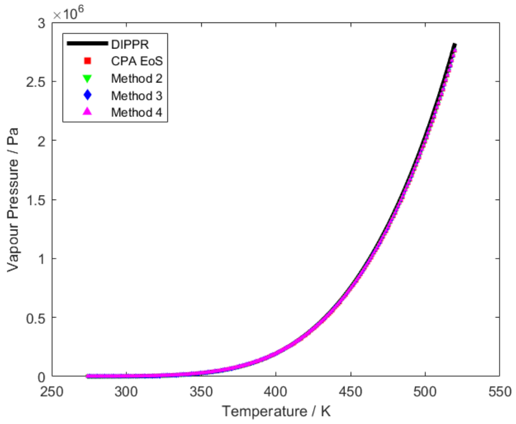

Fig. E.2: Vapour pressures predicted from the CPA EoS and from the three other methods for isobutanol, with an ADD of 0.9 % in the second method.

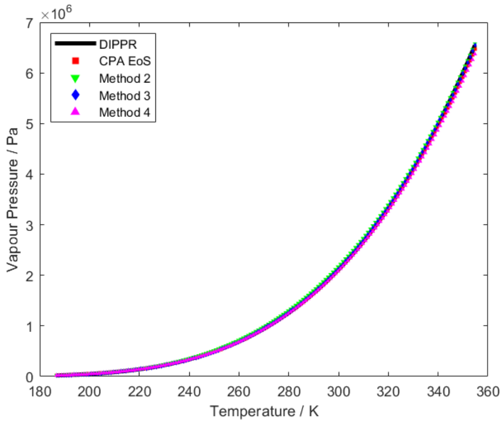

Fig. E.3: Vapour pressures predicted from the CPA EoS and from the three other methods for hydrogen sulfide, with an ADD of 0.6 % in the third method.

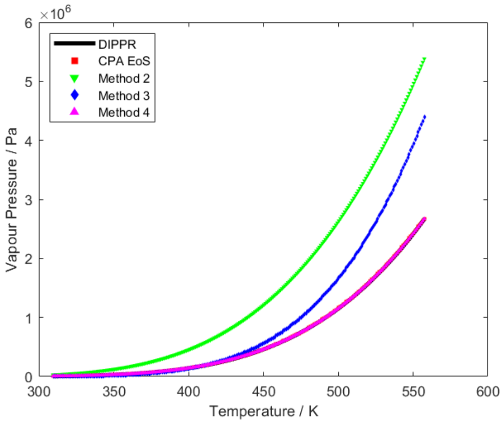

Fig. E.4: Vapour pressures predicted from the CPA EoS and from the three other methods for pyridine, with an ADD of 0.1 % in the fourth method.

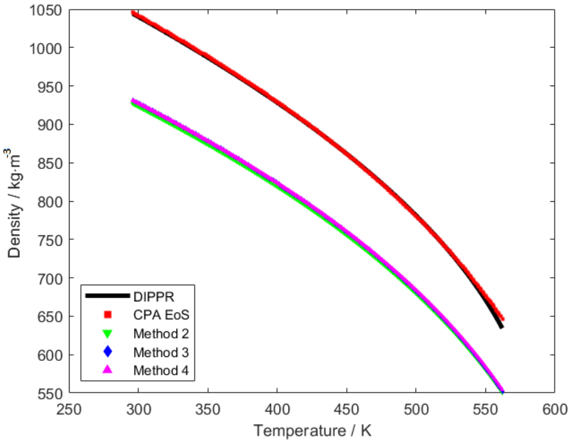

Fig. E.5: Liquid densities predicted from the CPA EoS and from the three other methods for acetic acid, with an ADD of 0.2 % in the CPA EoS.

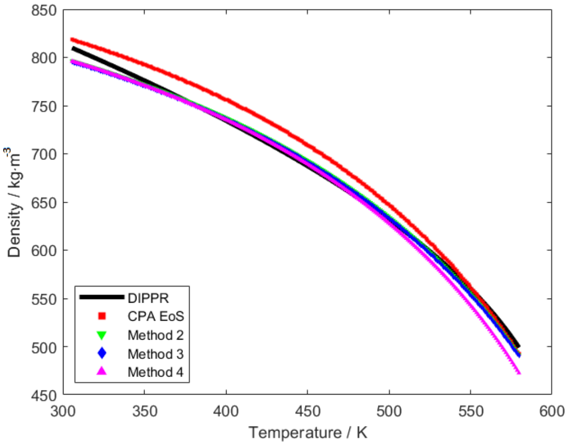

Fig. E.6: Liquid densities predicted from the CPA EoS and from the three other methods for 1-hexanol, with an ADD of 0.7 % in the second method.

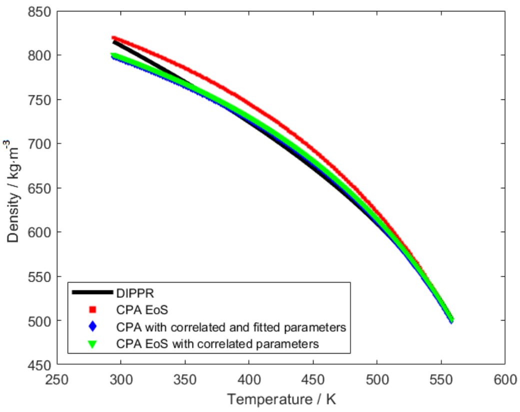

Fig. E.7: Liquid densities predicted from the CPA EoS and from the three other methods for 1-pentanol, with an ADD of 0.7 % in the third method.

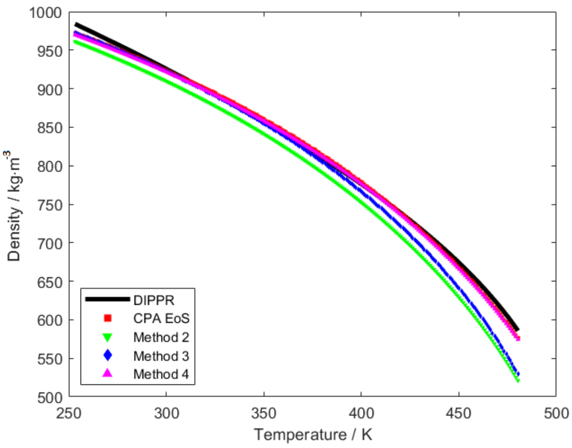

Fig. E.8: Liquid densities predicted from the CPA EoS and from the three other methods for methyl ethanoate, with an ADD of 0.6 % in the fourth method.

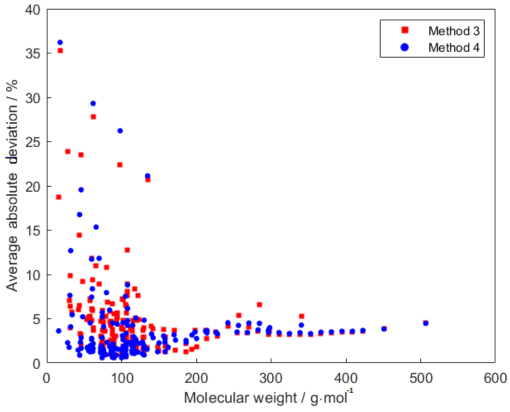

Fig. E.9: Average Absolute Deviations (AAD) in the calculation of liquid density following methods 3 and 4 with the molecular mass.

Predicting properties in pure compounds

Table E.1: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 1 of 7.

		Methods 2, 3 and 4	**Methods 2 and 3**	**Method 3**	**Method 4**	
Nr	**Compound**	$b^{\text{corr.}}$ / L · mol^{-1}	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
1	1,2-propylene glycol	0.073	2604.4	0.7	2396.9	1.0
2	1,3-butadiene	0.064	2473.5	0.4	2189.5	0.7
5	1-butanol	0.082	2710.8	0.6	2352.4	1.0
6	1-decanol	0.182	3432.8	1.2	3572.1	1.1
7	1-decene	0.168	3359.6	1.0	3246.4	1.1
8	1-dodecanol	0.218	3603.0	1.2	3911.1	1.0
9	1-heptanol	0.131	3131.5	1.1	3226.6	1.0
10	1-hexanol	0.114	3011.1	1.0	2919.3	1.0
11	1-hexene	0.101	2904.3	0.6	2569.8	0.9
13	1-octanol	0.148	3240.0	1.3	3335.8	1.2
14	1-octene	0.134	3155.0	0.8	2970.4	0.9
15	1-pentanol	0.098	2873.8	0.9	2810.2	0.9
16	1-propanol	0.066	2505.3	0.6	2218.9	0.9
17	2,2,4-trimethylpentane	0.140	3192.1	0.5	2779.7	0.9
18	2,4-dimethylhexane	0.140	3192.2	0.6	2840.9	0.9
19	2-butanol	0.085	2748.4	0.7	2547.5	0.9
20	2-butanone	0.077	2653.6	1.0	2859.1	0.8
21	2-butenal	0.066	2513.6	1.7	3253.9	0.7
22	2-heptanone	0.126	3096.1	1.1	3201.5	1.0
23	2-hexanone	0.109	2971.2	1.1	3080.5	1.0
24	2-methyl-1-propanol	0.082	2710.7	0.9	2710.7	0.9
25	2-methylheptane	0.140	3192.3	0.7	2906.1	1.0
26	2-methylhexane	0.123	3079.0	0.6	2739.1	0.9
27	2-methylpentane	0.107	2951.8	0.5	2553.2	0.8
28	2-methylpropane	0.075	2625.0	0.2	2078.2	0.7
29	2-methylpropene	0.069	2552.7	0.3	2141.2	0.7
30	2-methylpyridine	0.088	2782.8	1.3	3180.0	0.9

Table E.2: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 2 of 7.

		Methods 2, 3 and 4	**Methods 2 and 3**	**Method 3**	**Method 4**	
Nr	**Compound**	$b^{\text{corr.}}$ / L · mol^{-1}	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
31	2-octanol	0.152	3269.0	1.1	3142.0	1.2
32	2-octanone	0.142	3207.8	1.1	3312.7	1.1
33	2-pentanone	0.093	2827.3	1.0	2950.8	0.9
34	2-propanol	0.069	2550.8	0.4	1912.5	1.0
35	3-methylpentane	0.107	2951.8	0.5	2587.5	0.8
36	4-methyloctane	0.157	3295.7	0.8	3051.5	1.0
37	acetic acid	0.052	2265.4	0.5	2272.1	0.5
38	acetic anhydride	0.084	2738.6	1.6	3264.3	1.0
39	acetone	0.062	2438.4	0.0	1558.2	1.0
40	benzaldehyde	0.095	2849.6	1.6	3588.7	0.9
41	benzene	0.075	2636.9	1.0	2867.2	0.8
42	benzoic acid	0.102	2915.6	2.0	3778.2	1.4
43	benzyl alcohol	0.106	2948.6	1.3	3530.0	0.8
44	bis(chloromethyl)ether	0.074	2617.3	1.3	3048.0	0.9
45	bromine	0.046	2105.7	1.7	2858.4	0.6
46	butanal	0.077	2658.5	0.9	2790.2	0.8
47	butylamine	0.086	2753.7	0.4	2423.6	0.8
48	butylbenzene	0.142	3207.9	1.2	3437.9	1.0
49	carbon dioxide	0.032	1625.9	0.6	1491.2	0.8
50	carbonyl sulfide	0.036	1805.4	0.8	2066.3	0.5
51	cyanogenchloride	0.042	2000.7	1.4	2435.2	0.8
52	cyclohexane	0.096	2855.8	0.7	2840.3	0.8
53	diethanolamine	0.102	2908.6	1.3	2594.9	1.6
54	diethyl ether	0.080	2694.8	0.6	2411.9	0.8
55	diethylamine	0.087	2770.0	0.5	2410.7	0.9
56	diethylene glycol	0.095	2845.4	1.4	3418.0	0.8
57	diisopropyl ether	0.113	2999.6	0.5	2553.7	0.9

Predicting properties in pure compounds

Table E.3: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 3 of 7.

		Methods 2, 3 and 4	Methods 2 and 3	Method 3	Method 4	
Nr	**Compound**	$b^{\text{corr.}}$ / L · mol^{-1}	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
58	dimethyl carbonate	0.072	2593.8	1.2	2885.3	0.9
59	dimethyl disulfide	0.078	2668.1	1.2	3106.2	0.8
60	dimethyl ether	0.049	2189.5	0.6	2051.4	0.7
61	dimethyl sulfide	0.060	2405.9	0.9	2590.2	0.7
62	di-n-propyl-ether	0.113	2999.8	0.7	2758.7	0.9
63	dipropyl ether	0.113	2999.8	0.7	2695.8	1.0
64	ethane	0.043	2045.6	0.0	1542.7	0.6
65	ethanol	0.050	2220.7	0.6	2109.1	0.7
66	ethyl benzene	0.109	2971.4	1.1	3189.1	0.9
67	ethyl butyrate	0.115	3015.7	0.9	3033.7	0.9
68	ethyl decanoate	0.219	3606.2	1.5	3821.8	1.3
69	ethyl dodecanoate	0.256	3762.2	1.5	3807.5	1.5
70	ethyl ethanoate	0.082	2717.3	1.0	2735.8	0.9
71	ethyl hexadecanoate	0.333	4042.7	1.5	3763.9	1.7
72	ethyl isopentanoate	0.131	3135.5	0.9	2971.0	1.1
73	ethyl mercaptan	0.061	2420.8	0.9	2540.7	0.7
74	ethyl methanoate	0.037	1819.2	0.8	2134.0	0.4
75	ethyl octanoate	0.183	3436.3	1.4	3800.4	1.1
76	ethyl propanoate	0.098	2879.2	1.0	2852.6	1.0
77	ethyl propyl ether	0.096	2860.7	0.6	2643.9	0.8
78	ethyl tetradecanoate	0.294	3906.4	1.4	3752.3	1.5
79	ethylamine	0.054	2301.0	0.4	2040.1	0.7
80	ethylbenzene	0.109	2971.4	1.1	3189.1	0.9
81	ethylcyclohexane	0.127	3104.5	0.8	3110.6	0.8
82	glycerol	[g]	[g]	[g]	[g]	[g]
84	hexylbenzene	0.177	3404.9	1.3	3696.4	1.1

[g] Compound not considered in the calculations due to an extremely high AAD.

Table E.4: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 4 of 7.

		Methods 2, 3 and 4	**Methods 2 and 3**	**Method 3**	**Method 4**	
Nr	**Compound**	$b^{\mathrm{corr.}}$ / L · mol^{-1}	$\Gamma^{\mathrm{corr.}}$ / K	$c_1^{\mathrm{fit.}}$	$\Gamma^{\mathrm{fit.}}$ / K	$c_1^{\mathrm{fit.}}$
85	hydrogen bromide	0.029	1486.8	1.2	1813.2	0.6
86	hydrogen sulfide	0.031	1553.3	0.5	1570.1	0.5
87	i-butyl acetate	0.115	3015.7	0.9	2910.7	1.0
88	indole	0.103	2920.3	2.0	4203.4	0.9
89	isobutanal	0.077	2658.3	0.9	2718.4	0.8
90	isobutane	0.075	2625.0	0.2	2078.2	0.7
91	isobutanol	0.082	2710.7	0.9	2710.8	0.9
92	m-cresol	0.102	2907.9	1.4	3464.7	0.8
93	methane	0.028	1414.4	0.0	965.9	0.4
94	methanol	0.035	1758.5	0.1	1504.7	0.5
95	methyl bromide	0.044	2073.3	1.0	2371.2	0.6
96	methyl butyl ether	0.096	2860.7	0.7	2647.9	0.9
97	methyl butyrate	0.098	2879.2	1.0	2891.4	1.0
98	methyl decanoate	0.201	3523.2	1.3	3571.1	1.3
99	methyl diethanolamine	0.118	3037.5	0.7	2381.9	1.3
100	methyl dodecanoate	0.237	3685.7	1.4	3786.9	1.3
101	methyl ethanoate	0.066	2513.8	1.0	2647.5	0.9
102	methyl heptanoate	[f]	[f]	[f]	[f]	[f]
103	methyl hexadecanoate	0.313	3975.9	1.6	4050.7	1.5
104	methyl hexanoate	[f]	[f]	[f]	[f]	[f]
105	methyl mercaptan	0.045	2092.9	1.0	2407.3	0.6
106	methyl methacrylate	0.093	2827.1	1.0	2913.9	0.9
107	methyl methanoate	0.051	2239.8	1.1	2518.5	0.8
108	methyl nonanoate	[f]	[f]	[f]	[f]	[f]
109	methyl octadecanoate	0.353	4107.8	1.7	4190.9	1.6
110	methyl octanoate	0.165	3342.9	1.2	3423.9	1.2

[f] Compound not present in the DIADEM Professional database.

Table E.5: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 5 of 7.

		Methods 2, 3 and 4	Methods 2 and 3	Method 3	Method 4	
Nr	**Compound**	$b^{\text{corr.}}$ / L · mol^{-1}	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
111	methyl oleate	0.346	4085.6	1.7	4142.0	1.7
112	methyl pentadecanoate	f	f	f	f	f
113	methyl pentanoate	f	f	f	f	f
114	methyl propanoate	0.082	2717.3	1.0	2758.0	0.9
115	methyl tetradecanoate	0.274	3835.5	1.5	3902.5	1.4
116	methyl tridecanoate	f	f	f	f	f
117	methyl undecanoate	f	f	f	f	f
118	methylamine	0.039	1898.7	0.5	1790.7	0.6
119	methylcyclohexane	0.143	3208.8	0.5	2747.4	0.8
120	monoethanolamine	0.061	2429.3	1.1	2600.4	0.9
121	monoethylene glycol	0.072	2586.2	0.5	2253.2	0.8
122	m-xylene	0.111	2983.3	1.1	3203.0	0.9
123	n-butane	0.075	2625.2	0.3	2170.2	0.7
124	n-butyl acetate	0.115	3015.7	1.0	3050.8	1.0
125	n-butyl butyrate	f	f	f	f	f
126	n-butyl ethanoate	0.115	3015.7	1.1	3070.6	1.0
127	n-butyl mercaptan	0.092	2822.2	0.9	2965.6	0.8
128	n-butyl methanoate	0.099	2882.1	1.0	2910.1	1.0
129	n-butyl nonanoate	0.237	3685.7	1.2	3843.1	1.1
130	n-butyl octadecanoate	0.414	4294.3	1.5	4091.1	1.7
131	n-butyl pentanoate	0.165	3343.1	1.2	3305.1	1.2
132	n-butyl propanoate	0.131	3135.6	1.0	3077.8	1.1
133	n-decane	0.174	3391.7	1.0	3250.7	1.1
134	n-docosane	0.404	4264.8	1.6	4310.0	1.6
135	n-dodecane	0.210	3566.1	1.1	3488.2	1.2
136	n-dotriacontane	0.626	4813.7	2.0	4799.8	2.0

[f] Compound not present in the DIADEM Professional database.

Table E.6: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 6 of 7.

		Methods 2, 3 and 4	**Methods 2 and 3**	**Method 3**	**Method 4**	
Nr	**Compound**	$b^{\text{corr.}}$ / L · mol^{-1}	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
137	n-eicosane	0.363	4140.9	1.6	4161.4	1.5
138	n-heneicosane	0.383	4203.6	1.6	4244.5	1.6
139	n-heptacosane	0.511	4552.7	1.8	4586.5	1.8
140	n-heptane	0.123	3079.1	0.7	2800.1	0.9
141	n-hexacosane	0.489	4497.7	1.8	4532.1	1.8
142	n-hexadecane	0.284	3872.6	1.4	3863.7	1.4
143	n-hexane	0.107	2951.9	0.6	2629.8	0.8
144	n-hexatriacontane	0.722	5007.4	2.0	4999.8	2.0
145	nitrobenzene	0.098	2874.0	2.0	3971.4	0.9
146	nitrogen	0.027	1313.5	0.0	630.9	0.5
147	n-nonacosane	0.556	4660.0	1.9	4677.1	1.9
148	n-nonadecane	0.343	4076.1	1.5	4087.8	1.5
149	n-nonane	0.157	3295.8	0.9	3108.1	1.0
150	n-octacosane	0.534	4606.7	1.9	4632.5	1.8
151	n-octadecane	0.323	4010.2	1.5	4018.6	1.5
152	n-octane	0.140	3192.4	0.8	2968.0	1.0
153	n-pentacosane	0.468	4441.0	1.8	4465.3	1.7
154	n-pentadecane	0.265	3799.9	1.3	3780.7	1.3
155	n-pentane	0.090	2804.5	0.4	2414.3	0.8
160	n-propyl butyrate	[f]	[f]	[f]	[f]	[f]
161	n-propyl ethanoate	0.098	2879.2	1.0	2874.4	1.0
162	n-propyl mercaptan	0.076	2647.3	0.9	2955.6	0.6
163	n-propyl methanoate	0.083	2720.8	1.0	2782.4	0.9
164	n-propyl propanoate	0.115	3015.7	1.0	2972.8	1.0
165	n-tetracosane	0.446	4383.7	1.7	4421.2	1.7
166	n-tetradecane	0.247	3725.3	1.3	3688.0	1.3

[f] Compound not present in the DIADEM Professional database.

Table E.7: Correlated and fitted parameters used in the prediction of liquid density and vapour pressure by the four different methods - 7 of 7.

		Methods 2, 3 and 4	**Methods 2 and 3**	**Method 3**	**Method 4**	
Nr	**Compound**	$b^{\text{corr.}}$ / $\text{L} \cdot \text{mol}^{-1}$	$\Gamma^{\text{corr.}}$ / K	$c_1^{\text{fit.}}$	$\Gamma^{\text{fit.}}$ / K	$c_1^{\text{fit.}}$
167	n-triacontane	0.579	4712.3	1.9	4725.5	1.9
168	n-tricosane	0.425	4325.1	1.7	4346.8	1.7
169	n-undecane	0.192	3481.3	1.1	3372.3	1.1
170	o-cresol	0.102	2907.9	1.1	3117.5	0.9
172	oxygen	0.022	965.1	0.0	771.8	0.5
173	o-xylene	0.111	2983.3	1.1	3240.9	0.9
174	p-cresol	0.102	2907.9	1.5	3526.8	0.8
175	pentylbenzene	0.160	3310.0	1.2	3599.2	1.0
179	phenol	0.084	2735.1	1.0	2846.1	0.9
180	propane	0.059	2390.7	0.1	1920.7	0.6
181	propionic acid	0.068	2533.6	0.6	2457.8	0.7
182	propylbenzene	0.126	3096.2	1.1	3305.3	0.9
183	propylene	0.054	2290.0	0.2	1842.7	0.7
184	p-xylene	0.111	2983.3	1.1	3206.7	0.9
185	pyridine	0.071	2578.5	1.4	3176.6	0.8
186	s-trioxane	0.065	2496.5	1.8	3210.7	0.9
187	sulfuryl chloride	0.085	2744.3	0.7	2696.6	0.8
188	terephthalic acid	[g]	[g]	[g]	[g]	[g]
189	tert-butanol	0.082	2710.5	0.7	2494.9	0.9
190	tert-butyl mercaptan	0.092	2821.9	0.6	2638.4	0.8
191	tetraethylene glycol	0.174	3390.1	1.9	3789.5	1.6
192	tetrahydrothiophene	0.079	2678.1	0.8	2894.2	0.6
193	toluene	0.093	2827.4	1.0	3047.4	0.8
194	trichloromethane	0.068	2535.4	1.0	2717.8	0.8
195	triethylamine	0.119	3049.9	0.0	2007.1	0.8
196	triethylene glycol	0.134	3151.0	1.5	3567.9	1.2
197	water	0.021	874.8	0.6	781.5	0.8

[g] Compound not considered in the calculations due to an extremely high AAD.

Table E.8: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 1 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
1	1,2-propylene glycol	7.1	4.5	4.7	4.1
2	1,3-butadiene	1.1	8.0	4.9	1.7
5	1-butanol	1.3	3.5	2.4	1.5
6	1-decanol	0.7	1.1	1.2	1.3
7	1-decene	0.8	5.0	4.1	3.3
8	1-dodecanol	1.4	1.7	1.2	2.3
9	1-heptanol	2.9	1.5	2.2	2.9
10	1-hexanol	2.2	0.7	0.7	1.1
11	1-hexene	1.2	7.3	4.6	1.8
13	1-octanol	0.7	1.4	1.2	0.9
14	1-octene	0.8	5.6	3.9	2.4
15	1-pentanol	0.8	0.7	0.7	0.9
16	1-propanol	0.7	2.0	1.8	2.8
17	2,2,4-trimethylpentane	1.2	5.9	2.9	1.1
18	2,4-dimethylhexane	0.9	6.4	3.7	1.2
19	2-butanol	0.9	2.7	3.7	5.2
20	2-butanone	0.7	3.4	1.4	1.2
21	2-butenal	1.9	5.5	9.0	11.8
22	2-heptanone	0.7	1.0	1.2	1.4
23	2-hexanone	0.7	1.6	1.1	0.6
24	2-methyl-1-propanol	1.1	1.2	1.2	1.2
25	2-methylheptane	0.8	5.8	3.6	1.4
26	2-methylhexane	0.9	6.8	4.1	1.5
27	2-methylpentane	24.3	7.4	4.7	1.4

Table E.9: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 2 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
28	2-methylpropane	1.8	12.4	7.3	1.9
29	2-methylpropene	1.5	9.4	5.2	1.4
30	2-methylpyridine	0.6	9.5	4.9	0.9
31	2-octanol	1.2	3.3	4.0	4.8
32	2-octanone	1.7	1.0	1.6	2.3
33	2-pentanone	0.7	1.4	1.0	1.0
34	2-propanol	0.7	3.6	4.8	7.4
35	3-methylpentane	1.0	5.3	2.6	1.2
36	4-methyloctane	2.4	4.1	2.9	1.0
37	acetic acid	0.2	12.2	11.8	11.7
38	acetic anhydride	1.7	5.8	3.8	4.5
39	acetone	0.5	10.6	7.1	4.5
40	benzaldehyde	0.7	14.9	6.4	1.9
41	benzene	1.2	6.2	3.6	1.0
42	benzoic acid	1.1	13.2	7.6	1.2
43	benzyl alcohol	0.6	17.6	12.8	8.8
44	bis(chloromethyl)ether	0.6	5.6	4.8	4.3
45	bromine	2.2	23.7	10.8	7.9
46	butanal	2.3	3.8	3.1	1.7
47	butylamine	0.6	3.1	2.2	1.9
48	butylbenzene	0.7	2.6	1.8	1.6
49	carbon dioxide	0.9	12.9	14.4	16.8
50	carbonyl sulfide	1.5	7.8	11.0	15.3
51	cyanogenchloride	0.9	13.2	5.9	1.3

Table E.10: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 3 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
52	cyclohexane	1.5	5.8	5.8	6.0
53	diethanolamine	2.2	5.7	6.6	7.5
54	diethyl ether	1.1	8.7	5.9	2.9
55	diethylamine	0.6	4.6	2.9	1.6
56	diethylene glycol	2.1	8.2	4.6	2.3
57	diisopropyl ether	1.3	10.9	7.1	3.0
58	dimethyl carbonate	0.6	5.3	2.8	1.6
59	dimethyl disulfide	1.7	10.7	5.7	1.6
60	dimethyl ether	1.0	5.0	3.2	1.7
61	dimethyl sulfide	1.6	6.2	3.9	1.6
62	di-n-propyl-ether	1.0	6.9	4.8	2.7
63	dipropyl ether	1.0	6.9	4.8	2.6
64	ethane	1.7	12.6	7.0	1.8
65	ethanol	0.4	1.4	2.1	2.9
66	ethyl benzene	0.7	4.9	2.6	0.7
67	ethyl butyrate	1.2	1.5	1.9	2.0
68	ethyl decanoate	4.5	0.9	1.9	2.8
69	ethyl dodecanoate	7.1	1.8	3.0	3.3
70	ethyl ethanoate	0.6	1.2	1.2	1.3
71	ethyl hexadecanoate	10.9	7.1	6.6	4.5
72	ethyl isopentanoate	1.0	4.0	3.0	2.0
73	ethyl mercaptan	2.0	5.3	3.7	2.2
74	ethyl methanoate	0.7	30.3	23.5	19.6
75	ethyl octanoate	2.8	1.0	1.4	2.6

Table E.11: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 4 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
76	ethyl propanoate	0.9	2.5	1.8	1.6
77	ethyl propyl ether	0.6	8.7	6.6	4.5
78	ethyl tetradecanoate	9.4	5.8	5.3	4.2
79	ethylamine	1.0	3.7	3.3	2.3
80	ethylbenzene	0.7	4.9	2.6	0.7
81	ethylcyclohexane	1.0	2.4	2.2	2.2
82	glycerol	[g]	[g]	[g]	[g]
84	hexylbenzene	0.8	2.9	1.8	1.8
85	hydrogen bromide	2.6	13.1	6.8	2.3
86	hydrogen sulfide	0.5	6.1	5.7	5.4
87	i-butyl acetate	0.8	2.9	2.0	1.5
88	indole	0.8	19.5	8.4	1.1
89	isobutanal	1.5	1.4	1.9	1.3
90	isobutane	1.8	12.4	7.3	1.9
91	isobutanol	1.1	1.2	1.2	1.2
92	m-cresol	0.6	13.1	8.1	4.2
93	methane	2.3	22.9	18.7	3.6
94	methanol	0.5	7.2	9.9	12.7
95	methyl bromide	1.3	10.5	5.6	1.6
96	methyl butyl ether	1.3	5.8	3.8	2.2
97	methyl butyrate	0.9	0.9	0.8	0.7
98	methyl decanoate	1.3	2.3	2.2	2.5
99	methyl diethanolamine	1.6	4.4	5.1	5.1
100	methyl dodecanoate	2.1	2.5	2.8	3.4

[g] Compound not considered in the calculations due to an extremely high AAD.

Table E.12: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 5 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
101	methyl ethanoate	0.5	3.5	1.9	0.6
102	methyl heptanoate	[f]	[f]	[f]	[f]
103	methyl hexadecanoate	3.7	4.0	4.1	4.5
104	methyl hexanoate	[f]	[f]	[f]	[f]
105	methyl mercaptan	3.9	12.1	9.2	5.2
106	methyl methacrylate	0.8	1.5	1.1	0.7
107	methyl methanoate	0.6	10.4	6.1	2.7
108	methyl nonanoate	[f]	[f]	[f]	[f]
109	methyl octadecanoate	4.1	3.3	3.6	4.0
110	methyl octanoate	2.9	1.4	1.9	2.3
111	methyl oleate	4.9	4.1	3.4	3.7
112	methyl pentadecanoate	[f]	[f]	[f]	[f]
113	methyl pentanoate	[f]	[f]	[f]	[f]
114	methyl propanoate	0.9	0.9	0.9	0.6
115	methyl tetradecanoate	2.7	4.0	4.1	4.5
116	methyl tridecanoate	[f]	[f]	[f]	[f]
117	methyl undecanoate	[f]	[f]	[f]	[f]
118	methylamine	1.1	5.4	6.4	7.6
119	methylcyclohexane	1.0	20.0	22.4	26.2
120	monoethanolamine	3.3	10.7	9.4	8.4
121	monoethylene glycol	1.6	26.9	27.8	29.3
122	m-xylene	0.7	5.8	3.4	1.5
123	n-butane	3.7	9.5	5.3	1.3
124	n-butyl acetate	1.8	2.6	2.7	3.0

[f] Compound not present in the DIADEM Professional database.

Table E.13: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 6 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
125	n-butyl butyrate	[f]	[f]	[f]	[f]
126	n-butyl ethanoate	1.6	1.7	2.0	2.3
127	n-butyl mercaptan	1.6	2.2	2.0	0.7
128	n-butyl methanoate	0.7	1.0	1.1	1.1
129	n-butyl nonanoate	2.3	2.4	2.8	3.7
130	n-butyl octadecanoate	4.6	6.0	5.2	4.3
131	n-butyl pentanoate	0.9	3.0	3.0	2.7
132	n-butyl propanoate	0.9	2.5	1.9	1.6
133	n-decane	0.8	5.2	3.9	2.9
134	n-docosane	3.1	3.1	3.2	3.4
135	n-dodecane	1.1	4.2	3.7	3.2
136	n-dotriacontane	3.8	3.9	3.9	3.8
137	n-eicosane	2.5	3.5	3.6	3.7
138	n-heneicosane	3.0	3.1	3.3	3.5
139	n-heptacosane	3.4	3.3	3.4	3.5
140	n-heptane	0.7	6.1	3.9	1.5
141	n-hexacosane	3.3	3.3	3.3	3.5
142	n-hexadecane	1.8	3.6	3.5	3.5
143	n-hexane	0.7	6.8	4.2	1.4
144	n-hexatriacontane	4.5	4.5	4.5	4.5
145	nitrobenzene	2.2	16.7	4.9	2.2
146	nitrogen	2.4	26.7	23.9	2.3
147	n-nonacosane	3.6	3.5	3.5	3.6
148	n-nonadecane	2.2	3.3	3.4	3.4

[f] Compound not present in the DIADEM Professional database.

Table E.14: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 7 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
149	n-nonane	0.7	5.1	3.7	2.2
150	n-octacosane	3.8	3.6	3.5	3.6
151	n-octadecane	2.0	3.5	3.4	3.5
152	n-octane	0.7	5.6	3.7	1.9
153	n-pentacosane	3.1	3.2	3.2	3.3
154	n-pentadecane	1.6	3.9	3.7	3.6
155	n-pentane	1.2	8.3	4.7	1.4
160	n-propyl butyrate	[f]	[f]	[f]	[f]
161	n-propyl ethanoate	0.9	2.6	1.9	1.9
162	n-propyl mercaptan	1.8	2.5	1.9	1.5
163	n-propyl methanoate	0.9	1.1	1.2	0.8
164	n-propyl propanoate	0.7	2.3	2.0	1.7
165	n-tetracosane	3.0	3.2	3.3	3.4
166	n-tetradecane	2.2	4.0	3.7	3.5
167	n-triacontane	3.7	3.6	3.6	3.7
168	n-tricosane	2.8	3.2	3.2	3.3
169	n-undecane	0.9	4.6	3.8	3.0
170	o-cresol	0.8	9.4	7.6	6.2
172	oxygen	2.4	8.5	4.0	4.1
173	o-xylene	1.6	8.2	5.7	3.3
174	p-cresol	0.9	14.2	8.9	4.8
175	pentylbenzene	0.6	3.6	1.8	1.3
179	phenol	0.9	5.9	5.2	4.4
180	propane	1.9	11.5	6.5	0.9

[f] Compound not present in the DIADEM Professional database.

Predicting properties in pure compounds

Table E.15: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 8 of 8.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
181	propionic acid	0.7	4.5	5.1	5.7
182	propylbenzene	0.7	2.8	1.7	1.3
183	propylene	2.0	11.1	6.1	1.5
184	p-xylene	0.6	5.2	2.9	1.0
185	pyridine	0.6	11.8	5.3	0.9
186	s-trioxane	1.9	14.0	5.6	0.6
187	sulfuryl chloride	0.7	20.6	20.7	21.1
188	terephthalic acid	[g]	[g]	[g]	[g]
189	tert-butanol	1.6	3.7	2.7	1.0
190	tert-butyl mercaptan	2.1	4.7	2.3	1.8
191	tetraethylene glycol	7.2	1.3	1.6	3.2
192	tetrahydrothiophene	0.4	5.4	3.2	1.4
193	toluene	0.8	5.6	3.0	0.9
194	trichloromethane	1.1	7.4	4.8	2.6
195	triethylamine	0.5	11.0	7.2	3.1
196	triethylene glycol	3.6	4.7	1.4	2.3
197	water	1.1	34.8	35.3	36.2

[g] Compound not considered in the calculations due to an extremely high AAD.

Table E.16: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 1 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
1	1.2-propylene glycol	2.8	30.1	10.3	0.5
2	1.3-butadiene	1.4	49.8	19.1	0.4
5	1-butanol	2.4	50.4	20.1	2.4
6	1-decanol	0.8	27.3	7.1	0.5
7	1-decene	0.7	20.0	5.5	0.6
8	1-dodecanol	2.9	71.5	15.9	1.2
9	1-heptanol	2.4	29.6	5.6	0.9
10	1-hexanol	6.1	8.5	6.1	2.6
11	1-hexene	2.2	49.0	19.4	0.5
13	1-octanol	3.0	25.0	5.0	1.4
14	1-octene	1.5	33.9	10.2	1.1
15	1-pentanol	1.3	11.3	3.9	0.5
16	1-propanol	1.0	45.2	16.4	0.4
17	2.2.4-trimethylpentane	0.4	56.3	22.0	0.5
18	2.4-dimethylhexane	0.4	50.4	18.9	0.4
19	2-butanol	3.3	32.8	12.4	0.9
20	2-butanone	5.2	52.0	13.6	0.8
21	2-butenal	4.8	301.6	54.8	2.6
22	2-heptanone	2.1	18.4	6.1	1.3
23	2-hexanone	1.3	21.0	6.3	0.9
24	2-methyl-1-propanol	1.5	0.9	0.9	0.9
25	2-methylheptane	0.3	44.0	15.4	0.3
26	2-methylhexane	0.5	50.7	18.9	0.4
27	2-methylpentane	24.9	51.6	22.7	0.3

Table E.17: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 2 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
28	2-methylpropane	0.5	74.1	34.2	0.5
29	2-methylpropene	1.0	64.2	26.8	0.5
30	2-methylpyridine	0.6	111.8	23.1	0.4
31	2-octanol	0.5	20.7	7.4	0.8
32	2-octanone	2.0	25.6	6.1	1.4
33	2-pentanone	2.0	23.4	7.6	1.0
34	2-propanol	3.0	72.2	34.5	1.9
35	3-methylpentane	1.7	52.4	21.1	0.7
36	4-methyloctane	43.1	31.5	13.0	0.9
37	acetic acid	0.6	6.2	1.4	1.8
38	acetic anhydride	2.0	174.3	34.2	0.8
39	acetone	2.2	84.1	42.4	1.1
40	benzaldehyde	0.8	270.7	38.8	0.4
41	benzene	0.8	56.3	13.8	0.8
42	benzoic acid	1.4	460.8	69.5	1.5
43	benzyl alcohol	1.3	169.4	28.7	1.3
44	bis(chloromethyl)ether	0.7	135.7	28.4	0.8
45	bromine	0.7	386.8	39.9	2.2
46	butanal	22.5	17.1	7.9	0.3
47	butylamine	4.3	49.5	18.5	0.3
48	butylbenzene	0.6	53.8	12.5	0.4
49	carbon dioxide	1.7	34.1	15.9	3.1
50	carbonyl sulfide	9.3	62.0	27.0	4.5
51	cyanogenchloride	2.1	217.3	36.0	2.0

Table E.18: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 3 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
52	cyclohexane	10.0	2.2	2.1	1.2
53	diethanolamine	2.5	41.3	13.6	2.6
54	diethyl ether	0.8	48.8	17.9	0.9
55	diethylamine	0.4	54.7	21.1	0.5
56	diethylene glycol	1.7	151.4	29.8	1.5
57	diisopropyl ether	1.2	63.6	24.3	1.3
58	dimethyl carbonate	0.7	88.8	19.2	0.9
59	dimethyl disulfide	2.6	111.9	24.7	0.8
60	dimethyl ether	0.4	31.0	10.6	0.3
61	dimethyl sulfide	1.6	42.5	12.0	0.8
62	di-n-propyl-ether	0.5	40.6	13.7	0.5
63	dipropyl ether	4.1	43.2	16.7	1.6
64	ethane	0.3	79.9	40.0	0.7
65	ethanol	1.9	20.9	6.5	1.9
66	ethyl benzene	0.4	50.8	12.0	0.4
67	ethyl butyrate	1.4	8.3	1.5	0.6
68	ethyl decanoate	5.9	96.1	12.0	3.2
69	ethyl dodecanoate	10.2	61.4	4.4	4.1
70	ethyl ethanoate	0.9	3.1	1.3	0.9
71	ethyl hexadecanoate	6.8	22.5	11.5	2.3
72	ethyl isopentanoate	2.6	24.0	9.0	0.8
73	ethyl mercaptan	0.5	28.3	7.3	0.7
74	ethyl methanoate	1.3	158.8	24.1	2.5
75	ethyl octanoate	1.8	118.4	23.2	0.3

Predicting properties in pure compounds

Table E.19: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 4 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
76	ethyl propanoate	3.2	14.0	1.7	0.9
77	ethyl propyl ether	2.5	38.7	13.3	2.3
78	ethyl tetradecanoate	5.6	15.1	7.2	3.5
79	ethylamine	0.1	45.3	16.9	0.2
80	ethylbenzene	0.4	50.8	12.0	0.4
81	ethylcyclohexane	1.2	1.8	1.2	1.3
82	glycerol	^{g}	^{g}	^{g}	^{g}
84	hexylbenzene	1.3	70.1	15.3	1.4
85	hydrogen bromide	0.5	166.8	28.6	1.0
86	hydrogen sulfide	0.4	4.8	0.6	1.0
87	i-butyl acetate	0.9	20.1	5.9	0.8
88	indole	1.1	812.2	68.3	1.0
89	isobutanal	7.4	9.0	3.5	1.0
90	isobutane	0.5	74.1	34.2	0.5
91	isobutanol	1.4	0.9	0.9	0.9
92	m-cresol	0.3	160.2	29.2	0.5
93	methane	0.7	88.6	73.6	0.4
94	methanol	1.0	38.3	16.6	2.5
95	methyl bromide	1.3	92.7	21.7	0.6
96	methyl butyl ether	0.6	37.6	12.8	0.6
97	methyl butyrate	2.4	5.0	1.2	1.1
98	methyl decanoate	3.3	5.0	2.7	2.1
99	methyl diethanolamine	8.3	67.5	25.9	0.3
100	methyl dodecanoate	2.8	10.9	5.3	1.7

^{g} Compound not considered in the calculations due to an extremely high AAD.

Table E.20: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 5 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
101	methyl ethanoate	0.6	35.9	8.8	0.6
102	methyl heptanoate	f	f	f	f
103	methyl hexadecanoate	2.2	8.4	3.7	1.9
104	methyl hexanoate	f	f	f	f
105	methyl mercaptan	10.7	56.7	22.5	1.4
106	methyl methacrylate	2.9	13.7	5.1	2.3
107	methyl methanoate	0.5	91.8	20.0	0.7
108	methyl nonanoate	f	f	f	f
109	methyl octadecanoate	1.6	17.7	4.4	1.4
110	methyl octanoate	1.0	20.4	4.5	0.8
111	methyl oleate	25.0	21.8	3.5	1.4
112	methyl pentadecanoate	f	f	f	f
113	methyl pentanoate	f	f	f	f
114	methyl propanoate	2.8	2.8	2.4	1.2
115	methyl tetradecanoate	10.6	5.7	3.5	2.0
116	methyl tridecanoate	f	f	f	f
117	methyl undecanoate	f	f	f	f
118	methylamine	0.3	21.7	8.5	0.9
119	methylcyclohexane	0.8	55.1	26.3	4.8
120	monoethanolamine	2.6	40.1	7.9	1.6
121	monoethylene glycol	1.7	32.7	16.3	2.7
122	m-xylene	0.2	52.5	12.1	0.3
123	n-butane	0.4	65.9	28.6	0.4
124	n-butyl acetate	12.2	3.9	2.5	0.5

[f] Compound not present in the DIADEM Professional database.

Table E.21: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 6 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
125	n-butyl butyrate	[f]	[f]	[f]	[f]
126	n-butyl ethanoate	13.3	8.5	3.6	1.1
127	n-butyl mercaptan	6.0	11.5	8.2	1.1
128	n-butyl methanoate	0.4	5.7	1.8	0.4
129	n-butyl nonanoate	6.0	19.8	9.7	4.2
130	n-butyl octadecanoate	3.2	35.4	8.4	1.3
131	n-butyl pentanoate	2.5	2.9	2.1	1.6
132	n-butyl propanoate	0.5	12.4	3.3	0.6
133	n-decane	2.4	29.0	7.1	0.7
134	n-docosane	8.3	11.3	3.4	2.5
135	n-dodecane	0.7	13.9	3.7	1.0
136	n-dotriacontane	4.7	5.1	4.4	4.5
137	n-eicosane	1.2	7.5	2.3	1.6
138	n-heneicosane	9.1	12.2	2.7	1.7
139	n-heptacosane	1.2	7.7	1.4	0.6
140	n-heptane	0.9	42.8	15.5	0.4
141	n-hexacosane	1.2	8.7	2.0	1.0
142	n-hexadecane	2.2	1.6	1.0	1.2
143	n-hexane	1.4	48.3	18.7	0.8
144	n-hexatriacontane	8.7	16.0	13.8	15.6
145	nitrobenzene	1.8	622.1	59.6	1.8
146	nitrogen	0.6	99.1	97.9	1.0
147	n-nonacosane	3.7	4.5	4.0	3.8
148	n-nonadecane	0.9	2.5	1.6	1.3

[f] Compound not present in the DIADEM Professional database.

Table E.22: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 7 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
149	n-nonane	0.5	31.3	9.8	0.6
150	n-octacosane	19.0	15.3	2.8	2.3
151	n-octadecane	0.5	1.1	1.1	0.9
152	n-octane	0.7	37.8	12.1	0.4
153	n-pentacosane	1.4	6.3	2.2	1.6
154	n-pentadecane	0.5	4.9	0.6	0.8
155	n-pentane	0.4	59.0	23.4	0.3
160	n-propyl butyrate	[f]	[f]	[f]	[f]
161	n-propyl ethanoate	7.6	12.3	1.1	1.2
162	n-propyl mercaptan	18.0	23.4	20.0	5.8
163	n-propyl methanoate	2.1	8.3	3.7	1.3
164	n-propyl propanoate	1.4	6.7	2.2	1.0
165	n-tetracosane	1.3	9.5	2.4	1.2
166	n-tetradecane	1.1	7.0	1.6	1.1
167	n-triacontane	4.5	4.6	4.6	4.4
168	n-tricosane	1.2	4.3	2.0	1.4
169	n-undecane	0.8	18.5	5.4	1.1
170	o-cresol	3.8	43.6	9.9	1.0
172	oxygen	0.9	70.2	32.3	1.4
173	o-xylene	0.8	56.8	13.7	0.7
174	p-cresol	1.3	197.4	32.9	1.3
175	pentylbenzene	1.6	71.4	15.4	1.6
179	phenol	5.1	17.4	5.0	1.9
180	propane	7.1	72.1	32.6	0.7

[f] Compound not present in the DIADEM Professional database.

Table E.23: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical compound - part 8 of 8.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Nr	**Compound**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
181	propionic acid	0.7	12.5	4.9	0.7
182	propylbenzene	0.3	47.0	11.6	0.3
183	propylene	1.1	71.5	32.1	0.8
184	p-xylene	0.3	52.1	12.5	0.3
185	pyridine	0.5	214.1	34.9	0.1
186	s-trioxane	21.9	370.0	47.4	0.8
187	sulfuryl chloride	2.3	6.9	6.5	3.8
188	terephthalic acid	[g]	[g]	[g]	[g]
189	tert-butanol	11.1	40.6	12.9	0.7
190	tert-butyl mercaptan	2.1	35.9	11.4	1.4
191	tetraethylene glycol	3.5	103.7	20.5	0.8
192	tetrahydrothiophene	0.1	43.7	11.5	0.2
193	toluene	0.4	52.7	12.6	0.4
194	trichloromethane	0.8	48.0	11.0	0.9
195	triethylamine	0.2	86.1	50.7	0.6
196	triethylene glycol	34.9	194.4	21.4	2.8
197	water	0.7	14.2	11.0	6.9

[f] Compound not present in the DIADEM Professional database.

Table E.24: Average absolute deviations (AAD) for the liquid densities determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical family and overall.

		Liquid density			
		Method 1	Method 2	Method 3	Method 4
Chemical family	**Number of compounds**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
Alcohols	16	1.1	2.2	2.5	3.0
Alkanes	39	2.3	5.2	3.7	2.4
Alkenes	6	0.8	2.9	2.1	1.8
Amines	10	3.4	6.6	5.2	4.2
Aromatics	20	0.8	8.5	4.6	2.5
Esters	43	2.3	3.5	3.1	2.8
Ethers	8	0.9	7.0	4.9	3.0
Ketones	6	0.8	2.9	2.1	1.8
Polyols	5	4.1	9.0	7.9	8.1
Thiols	5	2.1	5.0	3.5	2.1
Associating	45	1.3	7.0	5.9	5.5
Non-associating	129	1.9	5.3	3.8	2.8
All	174	2.0	6.0	4.7	3.7

Table E.25: Average absolute deviations (AAD) for the vapour pressures determined using the CPA EoS with the parameters in this project's database (method 1), using two correlated parameters (method 2), using one fitted and two correlated parameters (method 3) and using one correlated and two fitted parameters (method 4), compared with experimental correlations per chemical family and overall.

		Vapour pressure			
		Method 1	Method 2	Method 3	Method 4
Chemical family	**Number of compounds**	**AAD / %**	**AAD / %**	**AAD / %**	**AAD / %**
Alcohols	16	2.7	31.9	10.3	1.3
Alkanes	39	4.6	36.2	12.4	1.8
Alkenes	6	2.5	36.7	13.0	1.1
Amines	10	4.4	70.2	20.8	0.7
Aromatics	21	1.2	170.5	23.7	0.9
Esters	43	4.4	29.7	6.2	1.4
Ethers	8	1.3	57.3	16.6	1.0
Ketones	6	2.5	36.9	13.0	1.1
Polyols	6	9.5	108.3	19.3	1.7
Thiols	5	7.1	30.3	13.2	2.1
Associating	45	3.5	73.5	15.7	1.3
Non-associating	129	3.8	60.1	12.9	1.4
All	174	3.7	59.4	14.1	1.5

Predicting properties in pure compounds

Appendix F

Studies of dependence in binary mixtures

In this appendix, additional data related to the Hudson-McCoubrey theory is presented.

From Table F.1 to Table F.16, a database organised by number of entry can be found comprising the binary interaction parameters (k_{ij}) from the literature, their respective experimental conditions, the cross-volumes (β^{cross}), the combining rules and the types of equilibrium for which they were obtained. The numbers of the entries respect the ones given in Appendix C. Following the same sorting logic, from Table F.17 to Table F.21, the ionisation potentials for each chemical species can be found.

Afterwards, from Table F.22 to Table F.30, the determined values of the binary interaction parameters can be found as well as the calculated exponents (n) in the first method, in which the ionisation potentials are considered.

Next, from Table F.31 to Table F.39, the binary interaction parameters can be observed as well as the calculated exponents (n) in the second method, in which the ionisation potentials are replaced by an approximate expression.

Lastly, some studies of dependence not present in the text may be observed analysing the relation of the co-volume and of the van der Waals volume with the ionisation potential and the relation of the binary interaction parameter and of the exponent n with measures of system asymmetries.

Table F.1: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 1 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	**T / K** **or P / kPa** (†)	β^{cross}	**Combining** **rule**	**Type**	**References**
1,2-PG	n-heptane	0.032	101.32†	0	h	LLE	[1]
1-butanol	ethyl methanoate	0.065	298.15	0	ECR	VLE	[2]
1-butanol	n-decane	0.015	358.15	0	h	VLE	[1]
1-butanol	n-decane	0.015	373.15	0	h	VLE	[1]
1-butanol	n-decane	0.015	388.15	0	h	VLE	[1]
1-butanol	n-hexane	0.012	298.15	0	h	VLE	[1]
1-butanol	n-hexane	0.012	323.15	0	h	VLE	[1]
1-butanol	n-hexane	0.012	333.15	0	h	VLE	[1]
1-butanol	n-octane	0	283.16	0	h	VLE	[1]
1-butanol	n-octane	0	293.19	0	h	VLE	[1]
1-butanol	n-octane	0	298.15	0	h	VLE	[1]
1-butanol	n-octane	0	308.09	0	h	VLE	[1]
1-butanol	propionic acid	-0.020	h	0	CR-1	VLE	[1]
1-butanol	water	-0.065	h	0	CR-1	LLE	[1]
1-dodecanol	water	-0.013	101.32†	0	CR-1	LLE	[3]
1-dodecanol	water	-0.113	h	0	CR-1	LLE	[3]
1-heptanol	carbon dioxide	-0.001	374.63	0	CR-1	VLE	[4]
1-heptanol	water	-0.042	101.32†	0	CR-1	LLE	[1]
1-octanol	n-decane	0.033	373.15	0	h	VLE	[1]
1-octanol	n-decane	0.033	383.15	0	h	VLE	[1]
1-octanol	n-decane	0.033	393.15	0	h	VLE	[1]
1-octanol	n-decane	0.033	413.15	0	h	VLE	[1]
1-octanol	n-dodecane	0.040	393.15	0	h	VLE	[1]
1-octanol	n-dodecane	0.040	413.15	0	h	VLE	[1]
1-octanol	n-undecane	0.040	393.15	0	h	VLE	[1]
1-octanol	n-undecane	0.040	413.15	0	h	VLE	[1]

h No provided information. PG - propylene glycol.

Studies of dependence in binary mixtures

Table F.2: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 2 of 16.

Compound 1	**Compound 2**	k_{ij}	***T* / K**	β^{cross}	**Combining**	**Type**	**References**
Smaller Nr	**Bigger Nr**		**or *P* / kPa** (†)		**rule**		
1-octanol	water	-0.059	^{h}	0	CR-1	LLE	[1]
1-pentanol	n-heptane	0.024	358.15	0	^{h}	VLE	[5]
1-pentanol	water	-0.037	^{h}	0	CR-1	LLE	[1]
1-propanol	carbon dioxide	0.058	312.00	0	^{h}	VLE	[6]
1-propanol	cyclohexane	0.029	298.15	0	CR-1	VLE	[7]
1-propanol	n-hexane	0.017	298.15	0	^{h}	VLE	[8]
1-propanol	n-hexane	0.017	323.15	0	CR-1	VLE	[8]
1-propanol	propionic acid	-0.039	^{h}	0	CR-1	VLE	[1]
1-propanol	water	-0.080	298.15	0	Elliott	VLE	[1]
1-propanol	water	-0.080	333.15	0	CR-1	VLE	[1]
1-propanol	water	-0.080	363.15	0	Elliott	VLE	[1]
2,2,4-TMP	ethanol	-0.017	298.15	0	CR-1	VLE	[9]
2,2,4-TMP	ethanol	-0.017	323.15	0	Elliott	VLE	[9]
2-butanol	cyclohexane	0.024	323.15	0	^{h}	VLE	[1]
2-butanol	cyclohexane	0.023	338.15	0	^{h}	VLE	[1]
2-butanol	cyclohexane	0.044	348.15	0	^{h}	VLE	[1]
2-butanol	n-heptane	0.012	338.15	0	^{h}	VLE	[1]
2-butanol	n-heptane	0.012	348.15	0	^{h}	VLE	[1]
2-butanol	water	-0.115	101.32†	0	CR-1	LLE	[1]
2-propanol	acetic acid	-0.085	^{h}	0	CR-1	VLE	[11,12]
2-propanol	cyclohexane	0.029	298.15	0	^{h}	VLE	[1]
2-propanol	cyclohexane	0.030	298.15	0	CR-1	VLE	[13]
2-propanol	cyclohexane	0.030	333.15	0	^{h}	VLE	[14]
2-propanol	n-hexane	0.017	298.15	0	^{h}	VLE	[1]
2-propanol	n-hexane	0.017	323.15	0	^{h}	VLE	[1]

^{h} No provided information. TMP - trimethylpentane.

Table F.3: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 3 of 16.

Compound 1	**Compound 2**	k_{ij}	T **/ K**	β^{cross}	**Combining**	**Type**	**References**
Smaller Nr	**Bigger Nr**		**or** P **/ kPa (†)**		**rule**		
2-propanol	n-hexane	0.030	323.15	0	^{h}	VLE	[15]
2-propanol	n-hexane	0.030	348.15	0	^{h}	VLE	[15]
2-propanol	propionic acid	-0.065	^{h}	0	CR-1	VLE	[1]
2-propanol	water	-0.160	298.15	0	Elliott	VLE	[1]
2-propanol	water	-0.160	353.15	0	Elliott	VLE	[1]
2-propanol	water	-0.160	423.15	0	Elliott	VLE	[1]
2-propanol	water	-0.160	473.15	0	Elliott	VLE	[1]
2-propanol	water	-0.160	523.15	0	Elliott	VLE	[1]
2-propanol	water	-0.160	548.15	0	Elliott	VLE	[1]
2-propanol	water	-0.092	298.15	0	CR-1	VLE	[9]
2-propanol	water	-0.066	353.15	0	CR-1	VLE	[9]
2-propanol	water	-0.051	423.15	0	CR-1	VLE	[9]
2-propanol	water	-0.062	473.15	0	CR-1	VLE	[9]
2-propanol	water	-0.081	523.15	0	CR-1	VLE	[9]
2-propanol	water	-0.082	548.15	0	CR-1	VLE	[9]
acetic acid	AA	-0.039	333.00	0	CR-1	VLE	[16,17]
acetic acid	AA	-0.039	353.00	0	CR-1	VLE	[16,17]
acetic acid	AA	-0.039	365.00	0	CR-1	VLE	[16,17]
acetic acid	benzene	0.035	293.15	0	^{h}	VLE	[18]
acetic acid	carbon dioxide	0.019	333.00	0	^{h}	VLE/LLE	[19]
acetic acid	cyclohexane	0.092	318.15	0	^{h}	VLE	[1]
acetic acid	cyclohexane	0.077	101.32†	0	^{h}	LLE	[1]
acetic acid	diethyl ether	0.040	^{h}	0.0692	^{h}	VLE/LLE	[20]
acetic acid	di-n-PE	-0.007	^{h}	0.0081	^{h}	VLE/LLE	[20]
acetic acid	ethanol	-0.018	^{h}	0	CR-1	VLE/LLE	[20]
acetic acid	ethyl ethanoate	-0.040	372.20	0	^{h}	VLE	[1]

^{h} No provided information. AA - acetic anhydride. PE - propyl ether.

Table F.4: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 4 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa** (†)	β^{cross}	**Combining rule**	**Type**	**References**
acetic acid	ethyl ethanoate	0.038	[h]	0.0473	[h]	VLE/LLE	[20]
acetic acid	i-butyl acetate	0.000	390.15	0	[h]	VLE	[1]
acetic acid	isobutanol	-0.004	[h]	0	CR-1	VLE	[11]
acetic acid	methane	0.160	298.15	0	[h]	VLE	[1]
acetic acid	methane	0.180	323.15	0	[h]	VLE	[1]
acetic acid	methane	0.200	348.15	0	[h]	VLE	[1]
acetic acid	methanol	-0.035	308.15	0	Elliott	VLE	[1]
acetic acid	ME	-0.036	[h]	0.0166	[h]	VLE/LLE	[20]
acetic acid	n-decane	0.041	101.32†	0	[h]	LLE	[1]
acetic acid	n-dodecane	0.038	101.32†	0	[h]	LLE	[1]
acetic acid	n-nonane	0.043	101.32†	0	[h]	LLE	[1]
acetic acid	n-octane	0.053	323.15	0	[h]	VLE	[1]
acetic acid	n-octane	0.064	343.15	0	[h]	VLE	[1]
acetic acid	n-octane	0.046	101.32†	0	[h]	LLE	[1]
acetic acid	n-undecane	0.039	101.32†	0	[h]	LLE	[1]
acetic acid	toluene	0.020	303.15	0	[h]	VLE	[21]
acetic acid	water	-0.223	372.80	0	[h]	VLE	[22]
acetone	cyclohexane	0.022	298.15	0	[h]	VLE	[23]
acetone	cyclohexane	0.022	323.15	0	[h]	VLE	[23]
acetone	methanol	-0.016	298.15	0	[h]	VLE	[1]
acetone	ME	0.007	293.15	0	[h]	VLE	[24]
acetone	MMA	0.011	350.00	0	[h]	VLE/LLE	[20]
acetone	n-butane	0.035	293.15	0	[h]	VLE	[23]
acetone	n-butane	0.035	313.15	0	[h]	VLE	[23]
acetone	n-hexane	0.019	293.15	0	[h]	VLE	[23]
acetone	n-hexane	0.019	308.15	0	[h]	VLE	[23]

[h] No provided information. ME - methyl ethanoate. MMA - methyl methacrylate.

Table F.5: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 5 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa** (†)	β^{cross}	**Combining rule**	**Type**	**References**
acetone	n-hexane	0.019	318.15	0	h	VLE	[23]
acetone	n-pentane	0.026	298.15	0	h	VLE	[23]
acetone	n-pentane	0.000	372.70	0	h	VLE	[23]
acetone	n-pentane	0.000	397.70	0	h	VLE	[23]
acetone	water	-0.146	298.15	0.4626	h	VLE	[23]
acetone	water	-0.120	298.12	0	CR-1	VLE	[23]
benzene	diethylene glycol	0.028	101.32†	0.0350	h	LLE	[10,25-27]
benzene	ethanol	0.022	298.15	0.0020	h	VLE	[28]
benzene	ethanol	0.022	318.15	0.0020	h	VLE	[29]
benzene	ethanol	0.022	328.22	0.0020	h	VLE	[30]
benzene	methanol	0.006	298.15	0.0100	h	VLE	[28,31]
benzene	methanol	0.006	308.15	0.0100	h	VLE	[32]
benzene	methanol	0.006	318.15	0.0100	h	VLE	[33]
benzene	methanol	0.006	328.15	0.0100	h	VLE	[32]
benzene	methanol	0.006	373.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	393.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	413.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	433.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	453.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	473.15	0.0100	h	VLE	[34]
benzene	methanol	0.006	493.15	0.0100	h	VLE	[35]
benzene	ETA	0.006	101.32†	0.0210	h	LLE	[36]
benzene	MEG	0.049	101.32†	0.0400	h	LLE	[10,25-27]
benzene	TEG	0.032	101.32†	0.0700	h	LLE	[10,25-27]
benzene	TEG	0.032	h	0	h	VLE/LLE	[37]
benzene	water	0.036	h	0	h	VLE/LLE	[37]

[h] No provided information. MEG - monoethylene glycol. TEG - triethylene glycol. ETA - monoethanolamine.

Studies of dependence in binary mixtures

Table F.6: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 6 of 16.

Compound 1 Smaller Nr	**Compound 2** Bigger Nr	k_{ij}	T / K or P / kPa	β^{cross}	**Combining rule**	**Type**	**References**
butanal	CO_2	-0.286	310.20	0.0162	h	VLE/LLE	[38]
CO_2	diethylene glycol	0.035	290.00	0	h	VLE	[39]
CO_2	ethanol	0.051	291.15	0	h	VLE	[6]
CO_2	ethyl decanoate	0.038	323.00	0	h	VLE/LLE	[19]
CO_2	ethyl dodecanoate	0.048	323.00	0	h	VLE/LLE	[19]
CO_2	ethyl ethanoate	-0.055	323.00	0	h	VLE/LLE	[19]
CO_2	ethyl octanoate	0.030	323.00	0	h	VLE/LLE	[19]
CO_2	ethyl propanoate	-0.041	323.00	0	h	VLE/LLE	[19]
CO_2	hydrogen sulfide	0.118	298.15	0	h	VLE/LLE	[40]
CO_2	methane	0.088	298.15	0	h	VLE/LLE	[40]
CO_2	methanol	0.027	290.00	0	h	VLE	[6]
CO_2	methanol	-0.070	298.15	0	h	VLE/LLE	[1]
CO_2	methyl dodecanoate	0.052	323.00	0	h	VLE/LLE	[19]
CO_2	methyl ethanoate	-0.008	298.15	0	h	VLE/LLE	[19]
CO_2	methyl hexadecanoate	0.065	323.00	0	h	VLE/LLE	[19]
CO_2	methyl mercaptan	0.091	310.00	0	h	VLE	[41]
CO_2	methyl octadecanoate	0.072	323.00	0	h	VLE/LLE	[19]
CO_2	methyl oleate	0.057	323.00	0	h	VLE/LLE	[19]
CO_2	MT	0.058	323.00	0	h	VLE/LLE	[19]
CO_2	monoethylene glycol	0.083	298.10	0	h	VLE	[6]
CO_2	nitrogen	-0.058	270.00	0	h	VLE/LLE	[40]
CO_2	oxygen	0.090	283.15	0	h	VLE/LLE	[40]
CO_2	triethylene glycol	0.035	290.00	0	h	VLE	[39]
CO_2	water	-0.023	298.15	0	h	VLE	[6]
CO_2	water	0.114	298.15	0.0196	h	VLE/LLE	[38]
COS	diethylene glycol	0.080	290.00	0	h	VLE	[39]

[h] No provided information. MT - methyl tetradecanoate. COS - carbonyl sulfide.

Table F.7: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 7 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa (†)**	β^{cross}	**Combining rule**	**Type**	**References**
carbonyl sulfide	MEG	0.100	290.00	0	h	VLE	[39]
carbonyl sulfide	triethylene glycol	0.080	290.00	0	h	VLE	[39]
cyclohexane	ethanol	0.033	298.15	0	h	VLE	[35]
cyclohexane	ethanol	0.033	323.15	0	h	VLE	[42]
cyclohexane	methanol	0.040	101.32†	0	h	LLE	[1]
cyclohexane	MEG	0.059	101.32†	0	h	LLE	[10,27]
cyclohexane	water	0.051	101.32†	0	h	LLE	[10]
diethanolamine	n-hexadecane	-0.088	101.32†	0	h	LLE	[36]
diethanolamine	propane	0.038	325.00	0	h	VLE	[43]
diethanolamine	propane	0.038	350.00	0	h	VLE	[43]
diethanolamine	propane	0.038	375.00	0	h	VLE	[43]
diethanolamine	propionic acid	-0.055	h	0	CR-1	VLE	[1]
diethylamine	ethanol	-0.130	313.15	0	h	VLE	[44]
diethylamine	methanol	-0.123	398.58	0	h	VLE	[44]
diethylamine	methanol	-0.201	297.97	0	h	VLE	[44]
diethylamine	n-heptane	-0.002	328.00	0	h	VLE	[44]
diethylamine	n-heptane	-0.003	308.00	0	h	VLE	[44]
diethylamine	n-hexane	-0.001	333.15	0	h	VLE	[44]
diethylamine	water	-0.291	329.95	0	h	VLE	[44]
DEG	n-heptane	0.065	101.32†	0	h	LLE	[1]
DEG	n-heptane	0.065	101.32†	0	h	LLE	[10,27]
DEG	toluene	0.046	101.32†	0.033	h	LLE	[10,27]
DEG	water	-0.115	393.15	0	h	VLE	[1]
DEG	water	-0.361	393.15	0	h	VLE	[1]
DEG	water	-0.115	393.15	0	h	VLE	[45]
diisopropyl ether	n-butane	0.0070	273.15	0	h	VLE	[46]

[h] No provided information. MEG - monoethylene glycol. DEG - diethylene glycol.

Table F.8: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 8 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa (†)**	β^{cross}	**Combining rule**	**Type**	**References**
DIPE	n-heptane	0.002	323.15	0	^{h}	VLE	[47]
DIPE	water	-0.224	101.32†	0	^{h}	LLE	[48]
dimethyl ether	ethanol	0.162	333.00	0	^{h}	VLE	[4]
dimethyl ether	methane	-0.003	282.60	0	^{h}	VLE	[49]
dimethyl ether	n-butane	-0.037	297.86	0	^{h}	VLE	[50]
dimethyl ether	water	-0.304	325.00	0	^{h}	VLE	[6]
dipropyl ether	n-heptane	0.008	343.15	0	^{h}	VLE	[51,52]
dipropyl ether	water	-0.177	101.32†	0.196	^{h}	LLE	[48]
ethane	hydrogen sulfide	0.085	^{h}	0	^{h}	VLE	[53,54]
ethane	MEG	0.145	298.15	0	^{h}	VLE	[26,55]
ethane	triethylene glycol	0.135	^{h}	0	^{h}	VLE/LLE	[37]
ethanol	cyclohexane	0.033	298.15	0	^{h}	VLE	[1]
ethanol	ethylamine	0.159	293.15	0	^{h}	VLE	[44]
ethanol	isobutane	0.018	308.60	0	^{h}	VLE	[1]
ethanol	isobutane	0.018	318.40	0	^{h}	VLE	[1]
ethanol	isobutane	0.018	363.50	0	^{h}	VLE	[1]
ethanol	ETA	-0.031	338.15	0	^{h}	VLE	[36]
ethanol	ETA	-0.029	358.15	0	^{h}	VLE	[36]
ethanol	n-dodecane	-0.031	101.32†	0	^{h}	LLE	[1]
ethanol	n-heptane	0.024	358.15	0	^{h}	VLE	[1]
ethanol	n-hexadecane	-0.040	101.32†	0	^{h}	LLE	[1]
ethanol	n-hexane	0.010	298.15	0	^{h}	VLE	[1]
ethanol	n-octane	-0.017	298.15	0	^{h}	VLE	[1]
ethanol	n-octane	-0.017	323.15	0	^{h}	VLE	[1]
ethanol	n-pentane	0.045	372.70	0	^{h}	VLE	[1]

^{h} No provided information. DIPE - diisopropyl ether. MEG - monoethylene glycol. ETA - monoethanolamine.

Table F.9: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 9 of 16.

Compound 1 Smaller Nr	**Compound 2** Bigger Nr	k_{ij}	T / K or P / kPa (†)	β^{cross}	**Combining rule**	**Type**	**References**
ethanol	n-pentane	0.045	397.70	0	[h]	VLE	[1]
ethanol	n-pentane	0.045	422.60	0	[h]	VLE	[1]
ethanol	n-tetradecane	-0.033	101.32†	0	[h]	LLE	[1]
ethanol	propane	0.038	325.00	0	[h]	VLE	[1]
ethanol	propane	0.038	350.00	0	[h]	VLE	[1]
ethanol	propane	0.038	375.00	0	[h]	VLE	[1]
ethanol	toluene	0.014	308.15	0.003	[h]	VLE	[57]
ethanol	toluene	0.014	318.15	0.003	[h]	VLE	[58]
ethanol	toluene	0.014	328.15	0.003	[h]	VLE	[57]
ethanol	toluene	0.014	338.15	0.003	[h]	VLE	[59]
ethanol	toluene	0.014	348.15	0.003	[h]	VLE	[59]
ethanol	water	-0.110	298.14	0	Elliott	VLE	[1]
ethanol	water	-0.110	333.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	343.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	363.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	423.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	473.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	523.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	598.15	0	Elliott	VLE	[1]
ethanol	water	-0.110	623.15	0	Elliott	VLE	[1]
ethanol	water	-0.051	298.14	0	CR-1	VLE	[9]
ethanol	water	-0.036	333.15	0	CR-1	VLE	[9]
ethanol	water	-0.041	343.15	0	CR-1	VLE	[9]
ethanol	water	-0.036	363.15	0	CR-1	VLE	[9]
ethanol	water	-0.038	423.15	0	CR-1	VLE	[9]
ethanol	water	-0.042	473.15	0	CR-1	VLE	[9]

[h] No provided information.

Table F.10: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 10 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa** (†)	β^{cross}	**Combining** **rule**	**Type**	**References**
ethanol	water	-0.042	523.15	0	CR-1	VLE	[9]
ethanol	water	-0.087	598.15	0	CR-1	VLE	[9]
ethanol	water	-0.103	623.15	0	CR-1	VLE	[9]
ethyl ethanoate	water	-0.213	298.15	0	CR-1	VLE	[6]
EPE	methanol	-0.099	310.00	0	^{h}	VLE	[60]
EPE	water	-0.191	101.32†	0.2617	^{h}	LLE	[48]
ethylamine	n-butane	0.025	273.15	0	^{h}	VLE	[44]
ethylamine	n-butane	0.024	293.15	0	^{h}	VLE	[44]
ethylamine	n-butane	0.023	233.15	0	^{h}	VLE	[44]
ethylamine	n-butane	0.023	218.15	0	^{h}	VLE	[44]
ethylamine	n-hexane	0.012	293.15	0	^{h}	VLE	[44]
ethylamine	n-hexane	0.013	273.15	0	^{h}	VLE	[44]
ethylamine	n-hexane	0.013	253.15	0	^{h}	VLE	[44]
ethylbenzene	MEG	0.013	^{h}	0	^{h}	VLE/LLE	[61]
ethylbenzene	TEG	0.050	^{h}	0	^{h}	VLE/LLE	[37]
ethylbenzene	water	-0.017	^{h}	0	^{h}	VLE/LLE	[37]
HBr	water	-2.312	298.15	0	^{h}	VLE	[62]
H_2S	methane	0.076	^{h}	0	^{h}	VLE	[53]
H_2S	methane	0.076	^{h}	0	^{h}	VLE/LLE	[40]
H_2S	methanol	0.022	^{h}	0	^{h}	VLE	[54]
H_2S	MEG	-0.025	298.10	0	^{h}	VLE	[6]
H_2S	propane	0.092	^{h}	0	^{h}	VLE	[53]
H_2S	TEG	-0.066	290.00	0	^{h}	VLE	[39]
H_2S	water	-0.010	^{h}	0	^{h}	VLE/LLE	[40]

^{h} No provided information. EPE - ethyl propyl ether. MEG - monoethylene glycol. TEG - triethylene glycol.

Table F.11: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 11 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa** (†)	β^{cross}	**Combining rule**	**Type**	**References**
isobutane	methanol	0.035	273.15	0	^{h}	VLE	[1]
isobutane	methanol	0.050	323.15	0	^{h}	VLE	[1]
isobutane	methanol	0.059	373.15	0	^{h}	VLE	[1]
isobutanol	n-heptane	0.022	298.15	0	^{h}	VLE	[1]
isobutanol	n-heptane	0.022	333.15	0	^{h}	VLE	[1]
isobutanol	n-hexane	0.024	298.15	0	^{h}	VLE	[1]
isobutanol	n-hexane	0.024	332.53	0	^{h}	VLE	[1]
isobutanol	water	-0.103	298.15	0	Elliott	VLE	[1]
isobutanol	water	-0.103	308.15	0	^{h}	VLE	[1]
isobutanol	water	-0.103	323.15	0	Elliott	VLE	[1]
isobutanol	water	-0.060	101.32†	0	CR-1	LLE	[1]
m-cresol	methane	-0.034	462.00	0	^{h}	VLE	[63]
m-cresol	n-decane	0.002	373.00	0	^{h}	VLE	[64]
m-cresol	n-nonane	0.006	373.00	0	^{h}	VLE	[65]
m-cresol	water	-0.050	290.00	0	Elliott	VLE	[66]
methane	methanol	0.010	^{h}	0	^{h}	VLE	[1]
methane	methyl mercaptan	0.079	293.15	0	^{h}	VLE	[41]
methane	MEG	0.179	298.15	0	^{h}	VLE	[26,55,56]
methane	MEG	0.134	101.32†	0	^{h}	LLE	[67]
methane	triethylene glycol	0.204	298.15	0	^{h}	VLE	[26,55,56]
methane	water	0.010	^{h}	0	^{h}	VLE	[68]
methanol	MMA	0.054	313.00	0	^{h}	VLE/LLE	[20]
methanol	n-butane	0.035	273.15	0	^{h}	VLE	[69]
methanol	n-butane	0.050	323.15	0	^{h}	VLE	[69]
methanol	n-butane	0.059	373.15	0	^{h}	VLE	[69]
methanol	n-decane	-0.010	^{h}	0	^{h}	LLE	[70-72]

^{h} No provided information. MEG - monoethylene glycol. MMA - methyl methacrylate.

Table F.12: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 12 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	***T* / K** **or *P* / kPa (†)**	β^{cross}	**Combining rule**	**Type**	**References**
methanol	n-heptane	0.005	101.32†	0	h	LLE	[1]
methanol	n-hexane	0.010	101.32†	0	h	LLE	[1]
methanol	n-nonane	-0.006	h	0	h	LLE	[70,71]
methanol	n-octane	0.000	h	0	h	LLE	[70]
methanol	n-pentane	0.051	372.70	0	h	VLE	[1]
methanol	n-pentane	0.051	397.70	0	h	VLE	[1]
methanol	n-pentane	0.051	422.60	0	h	VLE	[1]
methanol	n-pentane	0.013	101.32†	0	h	LLE	[1]
methanol	propane	0.026	293.05	0	h	VLE	[1]
methanol	propane	0.059	313.10	0	h	VLE	[1]
methanol	propane	0.067	352.20	0	h	VLE	[1]
methanol	propionic acid	0.001	298.15	0	CR-1	VLE	[1]
methanol	toluene	0.000	318.15	0.029	h	VLE	[42]
methanol	water	-0.090	298.15	0	Elliott	VLE	[1]
methanol	water	-0.090	333.15	0	Elliott	VLE	[1]
methanol	water	-0.090	373.15	0	Elliott	VLE	[1]
methanol	water	-0.090	423.15	0	Elliott	VLE	[1]
methanol	water	-0.090	473.15	0	Elliott	VLE	[1]
methanol	water	-0.090	523.15	0	Elliott	VLE	[1]
methanol	water	-0.094	298.18	0	CR-1	VLE	[9]
methanol	water	-0.055	333.15	0	CR-1	VLE	[9]
methanol	water	-0.051	373.15	0	CR-1	VLE	[9]
methanol	water	-0.021	423.15	0	CR-1	VLE	[9]
methanol	water	-0.018	473.15	0	CR-1	VLE	[9]
ME	TCM	-0.057	313.15	0	CR-1	VLE	[24]
ME	water	-0.235	298.15	0	CR-1	VLE	[6]

[h] No provided information. ME - methyl ethanoate. TCM - trichloromethane.

Table F.13: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 13 of 16.

Compound 1	**Compound 2**	k_{ij}	***T* / K**	β^{cross}	**Combining**	**Type**	**References**
Smaller Nr	**Bigger Nr**		**or *P* / kPa** (†)		**rule**		
methyl mercaptan	nitrogen	0.159	310.00	0	^{h}	VLE	[41]
MMA	water	-0.070	298.15	0.3266	^{h}	VLE/LLE	[20]
methylamine	n-butane	0.026	218.00	0	^{h}	VLE	[44]
methylamine	n-butane	0.028	233.00	0	^{h}	VLE	[44]
methylamine	n-butane	0.027	288.00	0	^{h}	VLE	[44]
methylamine	n-hexane	0.004	218.00	0	^{h}	VLE	[44]
methylamine	n-hexane	0.009	233.00	0	^{h}	VLE	[44]
methylamine	n-hexane	0.012	263.00	0	^{h}	VLE	[44]
methylamine	n-hexane	0.009	293.00	0	^{h}	VLE	[44]
methylcyclohexane	MEG	0.061	101.32†	0	^{h}	LLE	[1]
monoethanolamine	n-heptane	0.015	101.32†	0	^{h}	LLE	[36]
monoethanolamine	water	-0.165	298.15	0	^{h}	VLE	[36]
monoethanolamine	water	-0.165	333.15	0	^{h}	VLE	[36]
monoethanolamine	water	-0.165	353.15	0	^{h}	VLE	[36]
monoethanolamine	water	-0.165	^{h}	0	^{h}	VLE/LLE	[74]
MEG	n-heptane	0.047	101.32†	0	^{h}	LLE	[1]
MEG	n-heptane	0.047	101.32†	0	^{h}	LLE	[10,25-27]
MEG	n-hexane	0.058	330.15	0	^{h}	VLE	[73]
MEG	n-hexane	0.059	101.32†	0	^{h}	LLE	[1]
MEG	n-nonane	0.015	^{h}	0	^{h}	VLE/LLE	[61]
MEG	n-octane	0.000	101.32†	0	^{h}	LLE	[10,25-27]
MEG	propane	0.113	298.15	0	^{h}	VLE	[26,55,56]
MEG	toluene	0.051	101.32†	0.042	^{h}	LLE	[10,25-27]
MEG	water	-0.028	343.15	0	CR-1	VLE	[1]
MEG	water	-0.115	343.15	0	Elliott	VLE	[1]
MEG	water	-0.012	363.15	0	CR-1	VLE	[1]

^{h} No provided information. MMA - methyl methacrylate. MEG - monoethylene glycol.

Table F.14: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 14 of 16.

Compound 1 **Smaller Nr**	**Compound 2** **Bigger Nr**	k_{ij}	**T / K** **or P / kPa (†)**	β^{cross}	**Combining rule**	**Type**	**References**
MEG	water	-0.115	363.15	0	Elliott	VLE	[1]
MEG	water	-0.028	343.15	0	CR-1	VLE	[45]
MEG	water	-0.012	363.15	0	Elliott	VLE	[45]
m-xylene	water	-0.017	373.00	0.039	h	LLE	[75,76,77]
n-butane	TEG	0.113	h	0	h	VLE/LLE	[37]
n-butane	water	0.088	101.32†	0	h	LLE	[10]
n-butyl acetate	n-heptane	0.041	347.85	0	h	VLE	[1]
n-butyl acetate	water	-0.205	298.15	0	h	VLE	[6]
n-decane	p-cresol	-0.072	101.32†	0	h	LLE	[78]
n-decane	phenol	-0.300	393.15	0	h	VLE	[79]
n-decane	TEG	0.080	h	0	h	VLE/LLE	[37]
n-decane	water	-0.069	101.32†	0	h	LLE	[10]
n-decane	water	-0.066	h	0	h	VLE/LLE	[37]
n-dodecane	o-cresol	-0.072	428.15	0	h	VLE	[78]
n-dodecane	TEG	0.073	h	0	h	VLE/LLE	[37]
n-dodecane	water	-0.121	h	0	h	VLE/LLE	[37]
n-heptane	propionic acid	0.025	298.15	0	h	VLE	[1]
n-heptane	propionic acid	0.017	323.15	0	h	VLE	[1]
n-heptane	propionic acid	0.025	298.15	0	h	VLE	[80]
n-heptane	propionic acid	0.017	323.15	0	h	VLE	[80]
n-heptane	TG	0.101	101.32†	0	h	LLE	[1]
n-heptane	TG	0.075	101.32†	0	h	LLE	[10,25-27]
n-heptane	TEG	0.094	101.32†	0	h	LLE	[1]
n-heptane	TEG	0.110	101.32†	0	h	LLE	[10,25-27]
n-heptane	TEG	0.094	h	0	h	VLE/LLE	[37]
n-heptane	water	0.010	101.32†	0	h	LLE	[10]

[h] No provided information. MEG - monoethylene glycol. TG - tetraethylene glycol. TEG - triethylene glycol.

Table F.15: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 15 of 16.

Compound 1	**Compound 2**	k_{ij}	***T* / K**	β^{cross}	**Combining**	**Type**	**References**
Smaller Nr	**Bigger Nr**		**or *P* / kPa (†)**		**rule**		
n-heptane	water	0.010	^{h}	0	^{h}	VLE/LLE	[37]
n-hexane	TEG	0.070	^{h}	0	^{h}	VLE/LLE	[37]
n-hexane	water	0.036	101.32†	0	^{h}	LLE	[10]
n-hexane	water	0.036	^{h}	0	^{h}	VLE/LLE	[37]
nitrogen	water	-0.200	310.93	0	^{h}	VLE	[1]
n-nonane	TEG	0.090	^{h}	0	^{h}	VLE/LLE	[37]
n-nonane	water	-0.043	^{h}	0	^{h}	VLE/LLE	[37]
n-octane	TEG	0.097	^{h}	0	^{h}	VLE/LLE	[37]
n-octane	water	-0.017	101.32†	0	^{h}	LLE	[10]
n-octane	water	-0.017	^{h}	0	^{h}	VLE/LLE	[37]
n-pentane	TEG	0.105	^{h}	0	^{h}	VLE/LLE	[37]
n-pentane	water	0.062	101.32†	0	^{h}	LLE	[10]
n-pentane	water	0.062	^{h}	0	^{h}	VLE/LLE	[37]
n-undecane	TEG	0.076	^{h}	0	^{h}	VLE/LLE	[37]
n-undecane	water	-0.095	^{h}	0	^{h}	VLE/LLE	[37]
o-cresol	phenol	-0.050	428.15	0	^{h}	VLE	[78]
o-cresol	water	-0.115	350.00	0	^{h}	LLE	[48]
oxygen	water	0.426	423.53	0	^{h}	VLE	[1]
o-xylene	TEG	0.050	^{h}	0	^{h}	VLE/LLE	[37]
o-xylene	water	-0.017	^{h}	0	^{h}	VLE/LLE	[37]
propane	water	0.114	101.32†	0	^{h}	LLE	[10]
toluene	TEG	0.036	101.32†	0.032	^{h}	LLE	[10,25-27]
toluene	TEG	0.038	^{h}	0	^{h}	VLE/LLE	[37]

^{h} No provided information. TEG - triethylene glycol.

Table F.16: Binary interaction parameter (k_{ij}), experimental conditions, cross-volume (β^{cross}), combining rule and type of equilibrium for each chemical pair in the database - part 16 of 16.

Compound 1 Smaller Nr	**Compound 2** Bigger Nr	k_{ij}	T / K or P / kPa	β^{cross}	**Combining rule**	**Type**	**References**
toluene	water	0.010	^{h}	0	^{h}	VLE/LLE	[37]
TEG	water	-0.211	297.60	0	^{h}	VLE	[1]
TEG	water	-0.372	297.60	0	^{h}	VLE	[1]
TEG	water	-0.201	332.60	0	^{h}	VLE	[1]
TEG	water	-0.337	332.60	0	^{h}	VLE	[1]
TEG	water	-0.115	298.15	0	^{h}	VLE	[45]

[h] No provided information. TEG - triethylene glycol.

Table F.17: Ionisation potential (I) for all the chemical compounds in the database [81] - part 1 of 5.

Nr	**Compound**	I **/ eV**	**Nr**	**Compound**	I **/ eV**
1	1,2-propylene glycol	^{i}	15	1-pentanol	10.00
2	1,3-butadiene	^{i}	16	1-propanol	10.22
3	1,8-H-perfluorooctane	^{i}	17	2,2,4-trimethylpentane	9.86
4	1-Br-perfluorooctane	^{i}	18	2,4-dimethylhexane	^{i}
5	1-butanol	10.06	19	2-butanol	9.88
6	1-decanol	^{i}	20	2-butanone	9.38
7	1-decene	9.42	21	2-butenal	9.73
8	1-dodecanol	^{i}	22	2-heptanone	9.30
9	1-heptanol	9.84	23	2-hexanone	9.35
10	1-hexanol	9.89	24	2-methyl-1-propanol	10.12
11	1-hexene	9.44	25	2-methylheptane	9.84
12	1-H-perfluorooctane	^{i}	26	2-methylhexane	^{i}
13	1-octanol	^{i}	27	2-methylpentane	10.12
14	1-octene	9.43	28	2-methylpropane	10.57

[i] Value not found.

Studies of dependence in binary mixtures

Table F.18: Ionisation potential (I) for all the chemical compounds in the database [81] - part 2 of 5.

Nr	Compound	I / eV	Nr	Compound	I / eV
29	2-methylpropene	9.24	57	diisopropyl ether	9.20
30	2-methylpyridine	9.02	58	dimethyl carbonate	10.50
31	2-octanol	[i]	59	dimethyl disulfide	7.40
32	2-octanone	9.40	60	dimethyl ether	10.03
33	2-pentanone	9.38	61	dimethyl sulfide	8.69
34	2-propanol	10.12	62	di-n-propyl-ether	9.27
35	3-methylpentane	10.08	63	dipropyl ether	9.27
36	4-methyloctane	[i]	64	ethane	11.52
37	acetic acid	10.65	65	ethanol	10.47
38	acetic anhydride	10.00	66	ethyl benzene	8.77
39	acetone	9.71	67	ethyl butyrate	[i]
40	benzaldehyde	9.49	68	ethyl decanoate	[i]
41	benzene	9.25	69	ethyl dodecanoate	[i]
42	benzoic acid	9.47	70	ethyl ethanoate	10.01
43	benzyl alcohol	8.50	71	ethyl hexadecanoate	[i]
44	bis(chloromethyl)ether	[i]	72	ethyl isopentanoate	[i]
45	bromine	11.81	73	ethyl mercaptan	9.29
46	butanal	9.84	74	ethyl methanoate	10.61
47	butylamine	8.72	75	ethyl octanoate	[i]
48	butylbenzene	8.69	76	ethyl propanoate	10.00
49	carbon dioxide	13.77	77	ethyl propyl ether	9.45
50	carbonyl sulfide	11.17	78	ethyl tetradecanoate	[i]
51	cyanogenchloride	12.34	79	ethylamine	8.86
52	cyclohexane	9.86	80	ethylbenzene	8.77
53	diethanolamine	[i]	81	ethylcyclohexane	9.54
54	diethyl ether	9.51	82	glycerol	[i]
55	diethylamine	8.01	83	hexafluorobenzene	9.91
56	diethylene glycol	[i]	84	hexylbenzene	[i]

[i] Value not found.

Studies of dependence in binary mixtures

Table F.19: Ionisation potential (*I*) for all the chemical compounds in the database [81] - part 3 of 5.

Nr	Compound	*I* / eV	Nr	Compound	*I* / eV
84	hexylbenzene	[i]	112	methyl pentadecanoate	[i]
85	hydrogen bromide	11.66	113	methyl pentanoate	10.40
86	hydrogen sulfide	10.45	114	methyl propanoate	10.15
87	i-butyl acetate	[i]	115	methyl tetradecanoate	10.45
88	indole	7.76	116	methyl tridecanoate	[i]
89	isobutanal	9.71	117	methyl undecanoate	[i]
90	isobutane	10.57	118	methylamine	8.98
91	isobutanol	10.09	119	methylcyclohexane	9.64
92	m-cresol	8.29	120	monoethanolamine	8.96
93	methane	12.51	121	monoethylene glycol	10.16
94	methanol	10.85	122	m-xylene	8.56
95	methyl bromide	10.54	123	n-butane	10.53
96	methyl butyl ether	9.54	124	n-butyl acetate	10.00
97	methyl butyrate	10.06	125	n-butyl butyrate	[i]
98	methyl decanoate	[i]	126	n-butyl ethanoate	10.00
99	methyl diethanolamine	[i]	127	n-butyl mercaptan	9.14
100	methyl dodecanoate	[i]	128	n-butyl methanoate	10.50
101	methyl ethanoate	10.27	129	n-butyl nonanoate	[i]
102	methyl heptanoate	[i]	130	n-butyl octadecanoate	[i]
103	methyl hexadecanoate	[i]	131	n-butyl pentanoate	[i]
104	methyl hexanoate	[i]	132	n-butyl propanoate	[i]
105	methyl mercaptan	9.44	133	n-decane	9.65
106	methyl methacrylate	9.70	134	n-docosane	[i]
107	methyl methanoate	10.81	135	n-dodecane	[i]
108	methyl nonanoate	[i]	136	n-dotriacontane	[i]
109	methyl octadecanoate	[i]	137	n-eicosane	[i]
110	methyl octanoate	[i]	138	n-heneicosane	[i]
111	methyl oleate	[i]	139	n-heptacosane	[i]

[i] Value not found.

Table F.20: Ionisation potential (I) for all the chemical compounds in the database [81] - part 4 of 5.

Nr	**Compound**	***I* / eV**	**Nr**	**Compound**	***I* / eV**
140	n-heptane	9.92	164	n-propyl propanoate	[i]
141	n-hexacosane	[i]	165	n-tetracosane	[i]
142	n-hexadecane	[i]	166	n-tetradecane	[i]
143	n-hexane	10.13	167	n-triacontane	[i]
144	n-hexatriacontane	[i]	168	n-tricosane	[i]
145	nitrobenzene	9.86	168	n-tricosane	[i]
146	nitrogen	15.58	169	n-undecane	9.56
147	n-nonacosane	[i]	170	o-cresol	8.14
148	n-nonadecane	[i]	171	octafluorotoluene	9.90
149	n-nonane	9.72	172	oxygen	12.07
150	n-octacosane	[i]	173	o-xylene	8.56
151	n-octadecane	[i]	174	p-cresol	8.13
152	n-octane	9.82	175	pentylbenzene	[i]
153	n-pentacosane	[i]	176	perfluorodecalin	[i]
154	n-pentadecane	[i]	177	perfluoromethylcyclohexane	[i]
155	n-pentane	10.35	178	perfluorotoluene	9.90
156	n-perfluoroheptane	[i]	179	phenol	8.47
157	n-perfluorohexane	[i]	180	propane	10.95
158	n-perfluorononane	[i]	181	propionic acid	10.52
159	n-perfluorooctane	[i]	182	propylbenzene	8.72
160	n-propyl butyrate	[i]	183	propylene	9.73
161	n-propyl ethanoate	10.04	184	p-xylene	8.44
162	n-propyl mercaptan	9.19	185	pyridine	9.25
163	n-propyl methanoate	10.52	186	s-trioxane	10.30

[i] Value not found.

Table F.21: Ionisation potential (I) for all the chemical compounds in the database [81] - part 5 of 5.

Nr	Compound	I / eV	Nr	Compound	I / eV
186	s-trioxane	10.30	192	tetrahydrothiophene	8.47
187	sulfuryl chloride	12.05	193	toluene	8.82
188	terephthalic acid	9.86	194	trichloromethane	11.37
189	tert-butanol	9.97	195	triethylamine	7.49
190	tert-butyl mercaptan	9.03	196	triethylene glycol	[i]
191	tetraethylene glycol	[i]	197	water	12.61

[i] Value not found.

Table F.22: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 1 of 9.

Compound 1	Compound 2	n	k_{ij}
1,2-propylene glycol	n-heptane	[j]	0.032
1-butanol	ethyl methanoate	4.7	0.065
1-butanol	n-decane	3.6	0.015
1-butanol	n-hexane	6.2	0.012
1-butanol	propionic acid	-7.2	-0.020
1-butanol	water	2.4	-0.065
1-dodecanol	water	[j]	-0.013
1-heptanol	carbon dioxide	2.8	-0.001
1-heptanol	water	2.7	-0.042
1-octanol	n-decane	[j]	0.033
1-octanol	n-dodecane	[j]	0.040
1-octanol	n-undecane	[j]	0.040
1-octanol	water	[j]	-0.059
1-pentanol	n-heptane	12.2	0.024
1-pentanol	water	2.7	-0.037

[j] Not calculated due to missing ionisation potential(s).

Table F.23: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 2 of 9.

Compound 1	**Compound 2**	n	k_{ij}
1-propanol	carbon dioxide	4.7	0.058
1-propanol	cyclohexane	9.0	0.029
1-propanol	n-hexane	4.5	0.017
1-propanol	propionic acid	-37361787.0	-0.039
1-propanol	water	2.0	-0.080
2,2,4-trimethylpentane	ethanol	2.6	-0.017
2-butanol	cyclohexane	65.7	0.030
2-butanol	n-heptane	4.5	0.012
2-butanol	water	1.9	-0.115
2-propanol	acetic acid	-17.0	-0.085
2-propanol	cyclohexane	9.1	0.030
2-propanol	n-hexane	5.1	0.024
2-propanol	propionic acid	-62110036.5	-0.065
2-propanol	water	2.0	-0.085
acetic acid	acetic anhydride	0.6	-0.039
acetic acid	benzene	6.6	0.035
acetic acid	carbon dioxide	3.9	0.019
acetic acid	cyclohexane	7.9	0.085
acetic acid	diethyl ether	6.0	0.040
acetic acid	di-n-propyl-ether	2.7	-0.007
acetic acid	ethanol	-177.8	-0.018
acetic acid	ethyl ethanoate	2.9	-0.001
acetic acid	isobutanol	2.7	-0.004
acetic acid	methane	23.9	0.180
acetic acid	methanol	-1.9	-0.035
acetic acid	methyl ethanoate	-4.0	-0.036

[j] Not calculated due to missing ionisation potential(s).

Table F.24: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 3 of 9.

Compound 1	Compound 2	n	k_{ij}
acetic acid	n-decane	3.6	0.041
acetic acid	n-dodecane	[j]	0.038
acetic acid	n-nonane	3.7	0.043
acetic acid	n-octane	4.1	0.054
acetic acid	n-undecane	3.5	0.039
acetic acid	toluene	3.8	0.020
acetic acid	water	-0.8	-0.223
acetone	cyclohexane	6.0	0.022
acetone	methanol	2.0	-0.016
acetone	methyl ethanoate	15.4	0.007
acetone	methyl methacrylate	4.3	0.011
acetone	n-butane	24.6	0.035
acetone	n-hexane	4.3	0.019
acetone	n-pentane	6.4	0.026
acetone	water	1.3	-0.133
benzene	diethylene glycol	[j]	0.028
benzene	ethanol	5.7	0.022
benzene	methanol	3.1	0.006
benzene	monoethanolamine	4.5	0.006
benzene	monoethylene glycol	11.3	0.049
benzene	triethylene glycol	[j]	0.032
benzene	water	3.2	0.036
butanal	carbon dioxide	-3.4	-0.286
carbon dioxide	diethylene glycol	[j]	0.035
carbon dioxide	ethanol	6.0	0.051
carbon dioxide	ethyl decanoate	[j]	0.038
carbon dioxide	ethyl dodecanoate	[j]	0.048

[j] Not calculated due to missing ionisation potential(s).

Table F.25: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 4 of 9.

Compound 1	**Compound 2**	n	k_{ij}
carbon dioxide	ethyl ethanoate	1.7	-0.055
carbon dioxide	ethyl octanoate	[j]	0.030
carbon dioxide	ethyl propanoate	2.2	-0.041
carbon dioxide	hydrogen sulfide	618.1	0.118
carbon dioxide	methane	539.8	0.088
carbon dioxide	methanol	32.9	0.027
carbon dioxide	methyl dodecanoate	[j]	0.052
carbon dioxide	methyl ethanoate	2.4	-0.008
carbon dioxide	methyl hexadecanoate	[j]	0.065
carbon dioxide	methyl mercaptan	11.5	0.091
carbon dioxide	methyl octadecanoate	[j]	0.072
carbon dioxide	methyl oleate	[j]	0.057
carbon dioxide	methyl tetradecanoate	3.3	0.058
carbon dioxide	monoethylene glycol	7.6	0.083
carbon dioxide	nitrogen	-631.7	-0.058
carbon dioxide	oxygen	43.3	0.090
carbon dioxide	triethylene glycol	[j]	0.035
carbon dioxide	water	10.3	0.114
carbonyl sulfide	diethylene glycol	[j]	0.080
carbonyl sulfide	monoethylene glycol	43.3	0.100
carbonyl sulfide	triethylene glycol	[j]	0.080
cyclohexane	ethanol	5.2	0.033
cyclohexane	methanol	3.9	0.040
cyclohexane	monoethylene glycol	7.6	0.059
cyclohexane	water	3.4	0.051
diethanolamine	n-hexadecane	[j]	-0.087

[j] Not calculated due to missing ionisation potential(s).

Table F.26: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 5 of 9.

Compound 1	**Compound 2**	n	k_{ij}
diethanolamine	propane	j	0.038
diethanolamine	propionic acid	j	-0.055
diethylamine	ethanol	-7.3	-0.130
diethylamine	methanol	-0.9	-0.162
diethylamine	n-heptane	1.6	-0.002
diethylamine	n-hexane	-0.3	0.000
diethylamine	water	0.6	-0.291
diethylene glycol	n-heptane	j	0.065
diethylene glycol	toluene	j	0.046
diethylene glycol	water	j	-0.238
diisopropyl ether	n-butane	3.5	0.007
diisopropyl ether	n-heptane	9.1	0.002
diisopropyl ether	water	1.6	-0.224
dimethyl ether	ethanol	43036.9	0.162
dimethyl ether	methane	2.2	-0.003
dimethyl ether	n-butane	-3.4	-0.037
dimethyl ether	water	-1.6	-0.304
dipropyl ether	n-heptane	31.8	0.008
dipropyl ether	water	1.9	-0.177
ethane	hydrogen sulfide	17.2	0.085
ethane	monoethylene glycol	116.9	0.145
ethane	triethylene glycol	j	0.135
ethanol	ethylamine	672.5	0.159
ethanol	isobutane	5.5	0.018
ethanol	monoethanolamine	-67.2	-0.030
ethanol	n-dodecane	j	-0.031
ethanol	n-heptane	3.7	0.024

[j] Not calculated due to missing ionisation potential(s).

Table F.27: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 6 of 9.

Compound 1	**Compound 2**	n	k_{ij}
ethanol	n-hexadecane	[j]	-0.040
ethanol	n-hexane	3.4	0.010
ethanol	n-octane	2.6	-0.017
ethanol	n-pentane	5.9	0.045
ethanol	n-tetradecane	[j]	-0.033
ethanol	propane	37.6	0.038
ethanol	toluene	3.6	0.014
ethanol	water	1.1	-0.110
ethyl ethanoate	water	1.2	-0.213
ethyl propyl ether	methanol	1.2	-0.099
ethyl propyl ether	water	1.6	-0.191
ethylamine	n-butane	8.2	0.024
ethylamine	n-hexane	3.5	0.013
ethylbenzene	monoethylene glycol	3.5	0.013
ethylbenzene	triethylene glycol	[j]	0.050
ethylbenzene	water	2.8	-0.017
hydrogen bromide	water	-14.2	-0.409
hydrogen sulfide	methane	152983.1	0.076
hydrogen sulfide	methanol	154.6	0.022
hydrogen sulfide	monoethylene glycol	1.1	-0.025
hydrogen sulfide	propane	8.0	0.092
hydrogen sulfide	triethylene glycol	[j]	-0.066
hydrogen sulfide	water	-1.9	-0.098
isobutane	methanol	4.6	0.048
isobutanol	n-heptane	3.6	0.005
isobutanol	n-hexane	10.1	0.024
isobutanol	water	2.4	-0.060

[j] Not calculated due to missing ionisation potential(s).

Table F.28: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 7 of 9.

Compound 1	**Compound 2**	n	k_{ij}
m-cresol	methane	2.1	-0.034
m-cresol	n-decane	2.9	0.002
m-cresol	n-nonane	3.3	0.006
m-cresol	water	2.5	-0.050
methane	methanol	49.1	0.010
methane	methyl mercaptan	13.6	0.079
methane	monoethylene glycol	15.4	0.156
methane	triethylene glycol	[j]	0.204
methane	water	13.7	0.191
methanol	methyl methacrylate	4.1	0.054
methanol	n-butane	4.7	0.048
methanol	n-decane	2.9	-0.010
methanol	n-heptane	3.1	0.005
methanol	n-hexane	3.2	0.010
methanol	n-nonane	2.9	-0.006
methanol	n-octane	3.0	0.000
methanol	n-pentane	4.1	0.051
methanol	propane	6.3	0.051
methanol	propionic acid	3.0	0.001
methanol	toluene	2.9	0.000
methanol	water	0.0	-0.071
methyl ethanoate	trichloromethane	-95962.7	-0.057
methyl ethanoate	water	0.5	-0.235
methyl mercaptan	nitrogen	15.9	0.159
methyl methacrylate	water	2.4	-0.070
methylamine	n-butane	4.2	0.027
methylamine	n-hexane	3.1	0.008

[j] Not calculated due to missing ionisation potential(s).

Studies of dependence in binary mixtures

Table F.29: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 8 of 9.

Compound 1	**Compound 2**	n	k_{ij}
methylcyclohexane	monoethylene glycol	5.7	0.061
monoethanolamine	n-heptane	3.5	0.015
monoethanolamine	water	0.6	-0.165
monoethylene glycol	n-heptane	4.5	0.047
monoethylene glycol	n-hexane	5.7	0.059
monoethylene glycol	n-nonane	3.3	0.015
monoethylene glycol	n-octane	3.0	0.000
monoethylene glycol	propane	209.3	0.113
monoethylene glycol	toluene	6.6	0.051
monoethylene glycol	water	2.2	-0.047
m-xylene	water	2.8	-0.017
n-butane	triethylene glycol	[j]	0.113
n-butane	water	3.9	0.088
n-butyl acetate	n-heptane	360.6	0.041
n-butyl acetate	water	1.8	-0.205
n-decane	p-cresol	-1.8	-0.072
n-decane	phenol	-7.1	-0.300
n-decane	triethylene glycol	[j]	0.080
n-decane	water	2.7	-0.066
n-dodecane	o-cresol	[j]	-0.072
n-dodecane	triethylene glycol	[j]	0.073
n-dodecane	water	[j]	-0.121
n-heptane	propionic acid	4.1	0.021
n-heptane	tetraethylene glycol	[j]	0.088
n-heptane	triethylene glycol	[j]	0.099
n-heptane	water	3.0	0.009
n-hexane	triethylene glycol	[j]	0.070

[j] Not calculated due to missing ionisation potential(s).

Table F.30: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the first method - part 9 of 9.

Compound 1	**Compound 2**	n	k_{ij}
n-hexane	water	3.2	0.036
nitrogen	water	-10.4	-0.200
n-nonane	triethylene glycol	[j]	0.090
n-nonane	water	2.7	-0.043
n-octane	triethylene glycol	[j]	0.097
n-octane	water	2.9	-0.017
n-pentane	triethylene glycol	[j]	0.105
n-pentane	water	3.5	0.062
n-undecane	triethylene glycol	[j]	0.076
n-undecane	water	2.6	-0.095
o-cresol	phenol	-33.6	-0.050
o-cresol	water	[j]	-0.115
oxygen	water	87.7	0.426
o-xylene	triethylene glycol	[j]	0.050
o-xylene	water	2.8	-0.017
propane	water	4.6	0.114
toluene	triethylene glycol	[j]	0.037
toluene	water	2.9	0.009
triethylene glycol	water	[j]	-0.247

[j] Not calculated due to missing ionisation potential(s).

Table F.31: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 1 of 9.

Compound 1	**Compound 2**	n	k_{ij}
1,2-propylene glycol	n-heptane	8.1	0.032
1-butanol	ethyl methanoate	7.8	0.065
1-butanol	n-decane	6.6	0.015
1-butanol	n-hexane	9.2	0.012
1-butanol	propionic acid	-4.0	-0.020
1-butanol	water	5.4	-0.065
1-dodecanol	water	5.9	-0.013
1-heptanol	carbon dioxide	6.0	-0.001
1-heptanol	water	5.8	-0.042
1-octanol	n-decane	29.6	0.033
1-octanol	n-dodecane	13.0	0.040
1-octanol	n-undecane	17.9	0.040
1-octanol	water	5.7	-0.059
1-pentanol	n-heptane	15.2	0.024
1-pentanol	water	5.7	-0.037
1-propanol	carbon dioxide	8.0	0.058
1-propanol	cyclohexane	12.0	0.029
1-propanol	n-hexane	7.5	0.017
1-propanol	propionic acid	-37258611.3	-0.039
1-propanol	water	5.1	-0.080
2,2,4-trimethylpentane	ethanol	5.6	-0.017
2-butanol	cyclohexane	68.7	0.030
2-butanol	n-heptane	7.5	0.012
2-butanol	water	5.0	-0.115
2-propanol	acetic acid	-13.9	-0.085
2-propanol	cyclohexane	12.2	0.030

Table F.32: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 2 of 9.

Compound 1	**Compound 2**	n	k_{ij}
2-propanol	n-hexane	8.1	0.024
2-propanol	propionic acid	-61924810.7	-0.065
2-propanol	water	5.0	-0.085
acetic acid	acetic anhydride	3.6	-0.039
acetic acid	benzene	9.9	0.035
acetic acid	carbon dioxide	7.6	0.019
acetic acid	cyclohexane	11.0	0.085
acetic acid	diethyl ether	9.1	0.040
acetic acid	di-n-propyl-ether	5.8	-0.007
acetic acid	ethanol	-174.4	-0.018
acetic acid	ethyl ethanoate	5.9	-0.001
acetic acid	isobutanol	5.7	-0.004
acetic acid	methane	27.3	0.180
acetic acid	methanol	1.1	-0.035
acetic acid	methyl ethanoate	-1.0	-0.036
acetic acid	n-decane	6.6	0.041
acetic acid	n-dodecane	6.4	0.038
acetic acid	n-nonane	6.7	0.043
acetic acid	n-octane	7.1	0.054
acetic acid	n-undecane	6.5	0.039
acetic acid	toluene	7.1	0.020
acetic acid	water	2.3	-0.223
acetone	cyclohexane	9.0	0.022
acetone	methanol	5.1	-0.016
acetone	methyl ethanoate	19.1	0.007
acetone	methyl methacrylate	7.3	0.011
acetone	n-butane	28.1	0.035

Table F.33: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 3 of 9.

Compound 1	**Compound 2**	n	k_{ij}
acetone	n-hexane	7.3	0.019
acetone	n-pentane	9.4	0.026
acetone	water	4.4	-0.133
benzene	diethylene glycol	22.2	0.028
benzene	ethanol	9.0	0.022
benzene	methanol	6.2	0.006
benzene	monoethanolamine	7.5	0.006
benzene	monoethylene glycol	14.5	0.049
benzene	triethylene glycol	8.7	0.032
benzene	water	6.4	0.036
butanal	carbon dioxide	0.0	-0.286
carbon dioxide	diethylene glycol	6.6	0.035
carbon dioxide	ethanol	9.7	0.051
carbon dioxide	ethyl decanoate	6.3	0.038
carbon dioxide	ethyl dodecanoate	6.3	0.048
carbon dioxide	ethyl ethanoate	4.9	-0.055
carbon dioxide	ethyl octanoate	6.2	0.030
carbon dioxide	ethyl propanoate	5.4	-0.041
carbon dioxide	hydrogen sulfide	671.4	0.118
carbon dioxide	methane	549.6	0.088
carbon dioxide	methanol	46.5	0.027
carbon dioxide	methyl dodecanoate	6.3	0.052
carbon dioxide	methyl ethanoate	5.8	-0.008
carbon dioxide	methyl hexadecanoate	6.3	0.065
carbon dioxide	methyl mercaptan	16.4	0.091
carbon dioxide	methyl octadecanoate	6.3	0.072
carbon dioxide	methyl oleate	6.3	0.057

Table F.34: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 4 of 9.

Compound 1	**Compound 2**	n	k_{ij}
carbon dioxide	methyl tetradecanoate	6.3	0.058
carbon dioxide	monoethylene glycol	11.3	0.083
carbon dioxide	nitrogen	-608.0	-0.058
carbon dioxide	oxygen	47.2	0.090
carbon dioxide	triethylene glycol	6.4	0.035
carbon dioxide	water	13.4	0.114
carbonyl sulfide	diethylene glycol	9.0	0.080
carbonyl sulfide	monoethylene glycol	46.7	0.100
carbonyl sulfide	triethylene glycol	7.5	0.080
cyclohexane	ethanol	8.2	0.033
cyclohexane	methanol	6.9	0.040
cyclohexane	monoethylene glycol	10.6	0.059
cyclohexane	water	6.4	0.051
diethanolamine	n-hexadecane	4.4	-0.087
diethanolamine	propane	9.9	0.038
diethanolamine	propionic acid	-2.6	-0.055
diethylamine	ethanol	-3.6	-0.130
diethylamine	methanol	2.4	-0.162
diethylamine	n-heptane	5.6	-0.002
diethylamine	n-hexane	5.8	0.000
diethylamine	water	3.8	-0.291
diethylene glycol	n-heptane	23.0	0.065
diethylene glycol	toluene	5994363.2	0.046
diethylene glycol	water	4.3	-0.238
diisopropyl ether	n-butane	6.7	0.007
diisopropyl ether	n-heptane	14.8	0.002
diisopropyl ether	water	4.7	-0.224

Table F.35: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 5 of 9.

Compound 1	**Compound 2**	n	k_{ij}
dimethyl ether	ethanol	43097.4	0.162
dimethyl ether	methane	5.7	-0.003
dimethyl ether	n-butane	-0.3	-0.037
dimethyl ether	water	1.5	-0.304
dipropyl ether	n-heptane	37.0	0.008
dipropyl ether	water	4.9	-0.177
ethane	hydrogen sulfide	20.4	0.085
ethane	monoethylene glycol	121.3	0.145
ethane	triethylene glycol	9.0	0.135
ethanol	ethylamine	689.1	0.159
ethanol	isobutane	8.5	0.018
ethanol	monoethanolamine	-57.6	-0.030
ethanol	n-dodecane	5.6	-0.031
ethanol	n-heptane	6.7	0.024
ethanol	n-hexadecane	5.7	-0.040
ethanol	n-hexane	6.4	0.010
ethanol	n-octane	5.6	-0.017
ethanol	n-pentane	8.9	0.045
ethanol	n-tetradecane	5.7	-0.033
ethanol	propane	40.8	0.038
ethanol	toluene	6.9	0.014
ethanol	water	4.2	-0.110
ethyl ethanoate	water	4.3	-0.213
ethyl propyl ether	methanol	4.3	-0.099
ethyl propyl ether	water	4.7	-0.191
ethylamine	n-butane	12.1	0.024
ethylamine	n-hexane	6.6	0.013

Table F.36: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 6 of 9.

Compound 1	**Compound 2**	n	k_{ij}
ethylbenzene	monoethylene glycol	6.6	0.013
ethylbenzene	triethylene glycol	48.4	0.050
ethylbenzene	water	5.9	-0.017
hydrogen bromide	water	-11.2	-0.409
hydrogen sulfide	methane	161201.3	0.076
hydrogen sulfide	methanol	158.8	0.022
hydrogen sulfide	monoethylene glycol	4.1	-0.025
hydrogen sulfide	propane	11.0	0.092
hydrogen sulfide	triethylene glycol	5.2	-0.066
hydrogen sulfide	water	1.3	-0.098
isobutane	methanol	7.6	0.048
isobutanol	n-heptane	6.6	0.005
isobutanol	n-hexane	13.1	0.024
isobutanol	water	5.5	-0.060
m-cresol	methane	5.4	-0.034
m-cresol	n-decane	6.1	0.002
m-cresol	n-nonane	6.6	0.006
m-cresol	water	5.6	-0.050
methane	methanol	67.7	0.010
methane	methyl mercaptan	18.0	0.079
methane	monoethylene glycol	18.8	0.156
methane	triethylene glycol	8.7	0.204
methane	water	16.7	0.191
methanol	methyl methacrylate	7.2	0.054
methanol	n-butane	7.7	0.048
methanol	n-decane	5.9	-0.010
methanol	n-heptane	6.1	0.005

Table F.37: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 7 of 9.

Compound 1	**Compound 2**	n	k_{ij}
methanol	n-hexane	6.2	0.010
methanol	n-nonane	5.9	-0.006
methanol	n-octane	0.0	0.000
methanol	n-pentane	7.1	0.051
methanol	propane	9.3	0.051
methanol	propionic acid	6.0	0.001
methanol	toluene	0.0	0.000
methanol	water	3.1	-0.071
methyl ethanoate	trichloromethane	-93776.4	-0.057
methyl ethanoate	water	3.6	-0.235
methyl mercaptan	nitrogen	21.7	0.159
methyl methacrylate	water	5.5	-0.070
methylamine	n-butane	7.4	0.027
methylamine	n-hexane	6.2	0.008
methylcyclohexane	monoethylene glycol	8.8	0.061
monoethanolamine	n-heptane	6.5	0.015
monoethanolamine	water	3.8	-0.165
monoethylene glycol	n-heptane	7.5	0.047
monoethylene glycol	n-hexane	8.7	0.059
monoethylene glycol	n-nonane	6.3	0.015
monoethylene glycol	n-octane	6.0	0.000
monoethylene glycol	propane	213.5	0.113
monoethylene glycol	toluene	9.7	0.051
monoethylene glycol	water	5.3	-0.047
m-xylene	water	5.9	-0.017
n-butane	triethylene glycol	14.6	0.113
n-butane	water	6.9	0.088

Table F.38: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 8 of 9.

Compound 1	**Compound 2**	n	k_{ij}
n-butyl acetate	n-heptane	363.7	0.041
n-butyl acetate	water	4.8	-0.205
n-decane	p-cresol	1.4	-0.072
n-decane	phenol	-4.0	-0.300
n-decane	triethylene glycol	24.9	0.080
n-decane	water	5.7	-0.066
n-dodecane	o-cresol	3.4	-0.072
n-dodecane	triethylene glycol	12.9	0.073
n-dodecane	water	5.5	-0.121
n-heptane	propionic acid	7.2	0.021
n-heptane	tetraethylene glycol	33.4	0.088
n-heptane	triethylene glycol	3179.4	0.099
n-heptane	water	6.1	0.009
n-hexane	triethylene glycol	61.0	0.070
n-hexane	water	6.2	0.035
nitrogen	water	-7.0	-0.200
n-nonane	triethylene glycol	53.7	0.090
n-nonane	water	5.8	-0.042
n-octane	triethylene glycol	252.5	0.097
n-octane	water	5.9	-0.017
n-pentane	triethylene glycol	28.1	0.105
n-pentane	water	6.5	0.061
n-undecane	triethylene glycol	16.4	0.076
n-undecane	water	5.6	-0.095
o-cresol	phenol	-30.5	-0.050
o-cresol	water	5.2	-0.115
oxygen	water	90.7	0.426

Table F.39: Binary interaction parameters (k_{ij}), respective chemical pair and calculated exponent (n) using the second method - part 9 of 9.

Compound 1	**Compound 2**	n	k_{ij}
o-xylene	triethylene glycol	47.9	0.050
o-xylene	water	5.9	-0.016
propane	water	7.6	0.114
toluene	triethylene glycol	14.1	0.037
toluene	water	6.1	0.009
triethylene glycol	water	4.7	-0.247

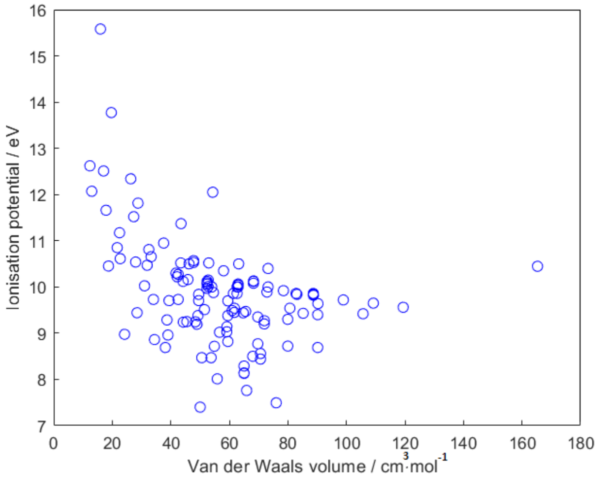

Fig. F.1: Study of dependence of the ionisation potential, I, with the van der Waals volume, V_w, for all the compounds.

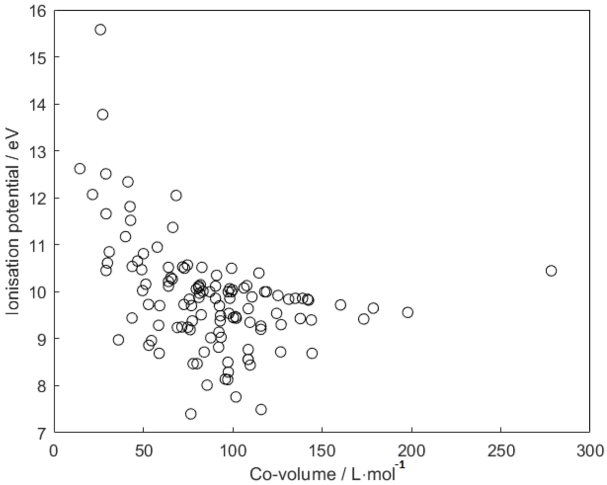

Fig. F.2: Study of dependence of the ionisation potential, I, with the co-volume, b, for all the compounds.

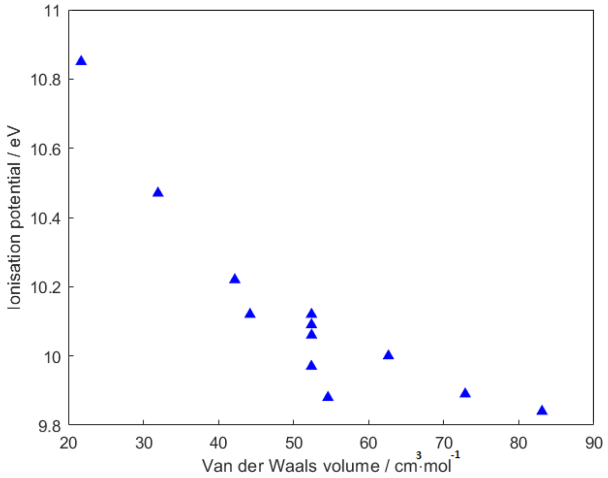

Fig. F.3: Study of dependence of the ionisation potential, I, with the van der Waals volume, V_w, in alcohols

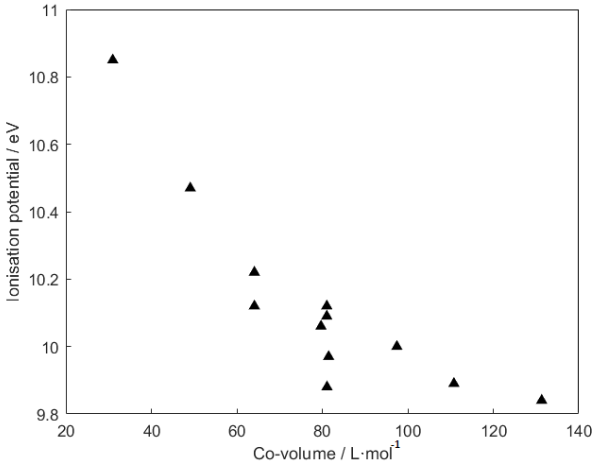

Fig. F.4: Study of dependence of the ionisation potential, I, with the co-volume, b, in alcohols.

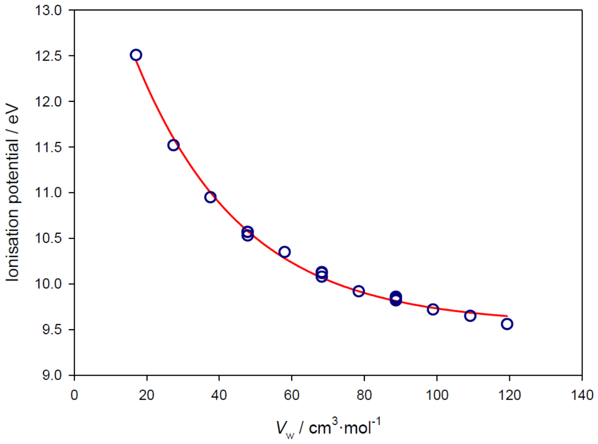

Fig. F.5: Study of dependence of the ionisation potential, I, with the co-volume, b, in alkanes. The regression (–) follows equation $I = 9.63 + 5.75 \cdot e^{-2.47 \cdot 10^{-2} \cdot b}$, with a determination coefficient of 0.9905.

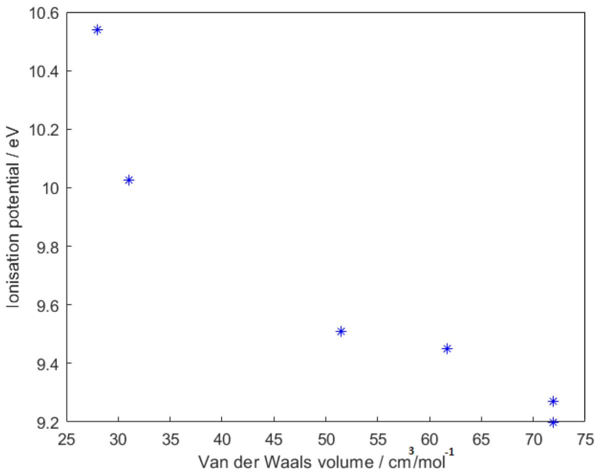

Fig. F.6: Study of dependence of the ionisation potential, I, with the van der Waals volume, V_w, in ethers.

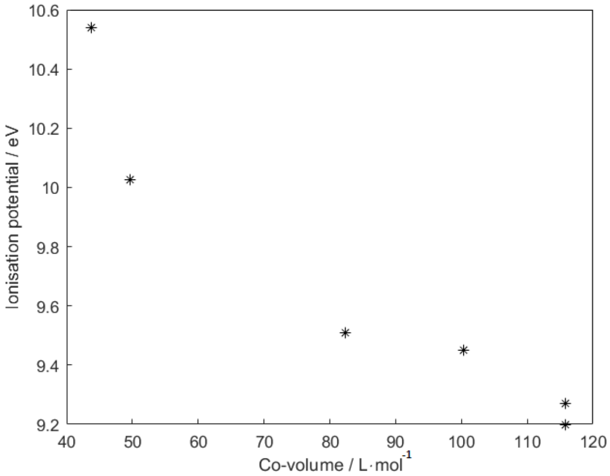

Fig. F.7: Study of dependence of the ionisation potential, I, with the co-volume, b, in ethers.

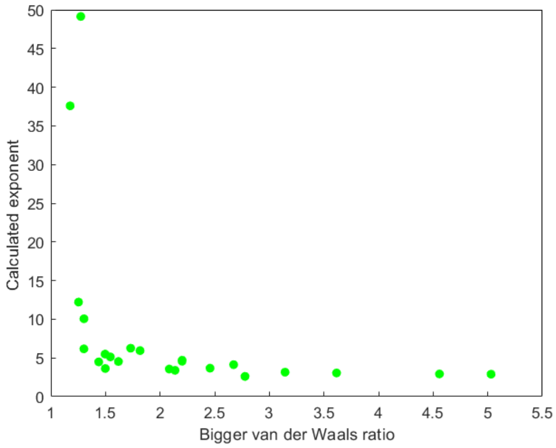

Fig. F.8: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alcohols-alkanes for the first method.

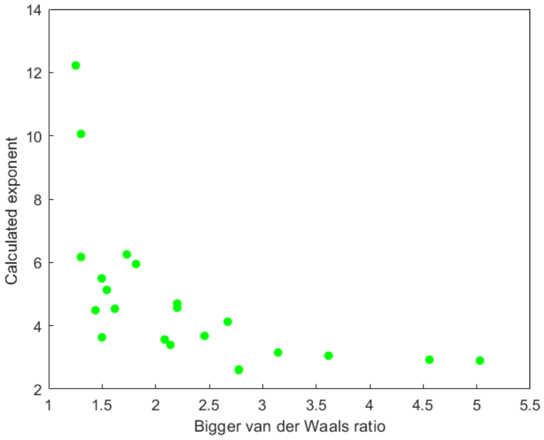

Fig. F.9: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alcohols-alkanes for the first method without extremely high values ($n > 20$).

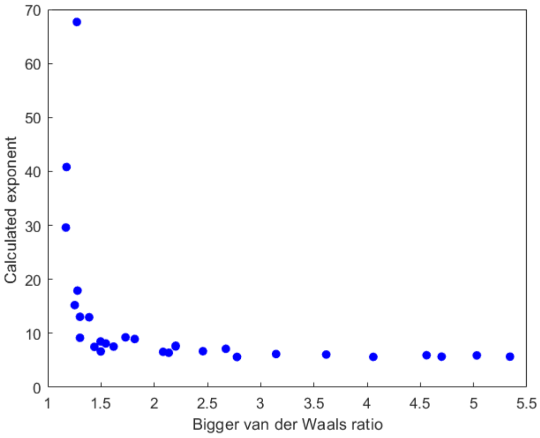

Fig. F.10: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alcohols-alkanes for the second method.

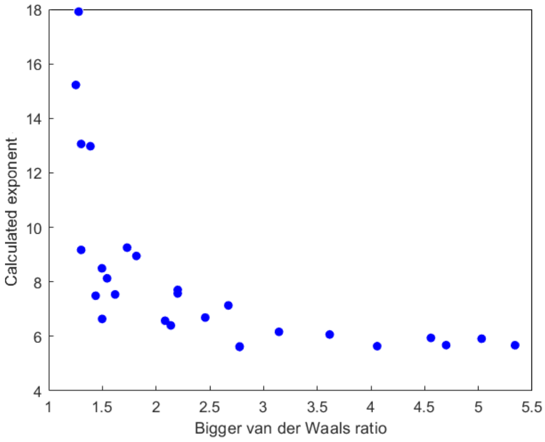

Fig. F.11: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alcohols-alkanes for the second method without extremely high values ($n > 20$).

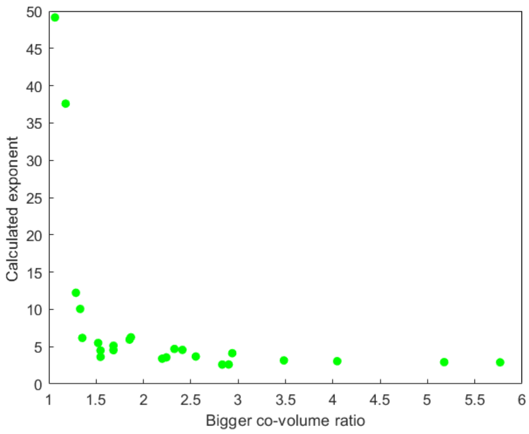

Fig. F.12: Study of dependence of the calculated exponent n with the ratio of co-volumes in alcohols-alkanes for the first method.

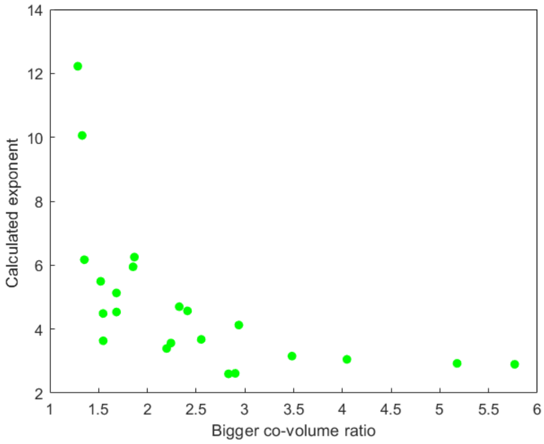

Fig. F.13: Study of dependence of the calculated exponent n with the ratio of co-volumes in alcohols-alkanes for the first method without extremely high values ($n > 20$).

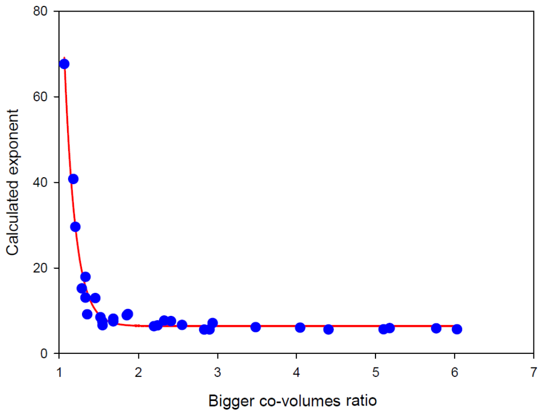

Fig. F.14: Study of dependence of the calculated exponent n with the ratio of co-volumes in alcohols-alkanes for the second method. The regression (–) follows equation $n = 6.42 + 1.32 \cdot 10^5 \cdot e^{-7.19 \cdot b_{\text{ratio}}}$, with a determination coefficient of 0.9732.

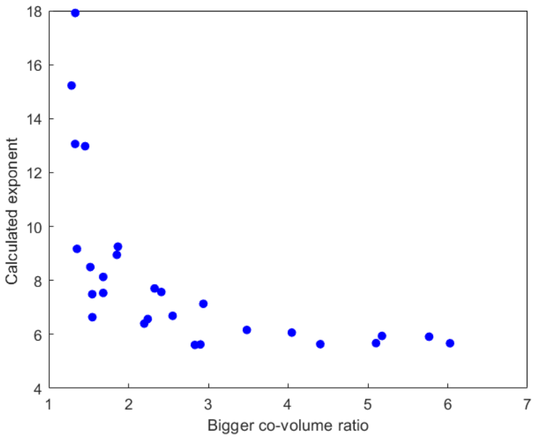

Fig. F.15: Study of dependence of the calculated exponent n with the ratio of co-volumes in alcohols-alkanes for the second method without extremely high values ($n > 20$).

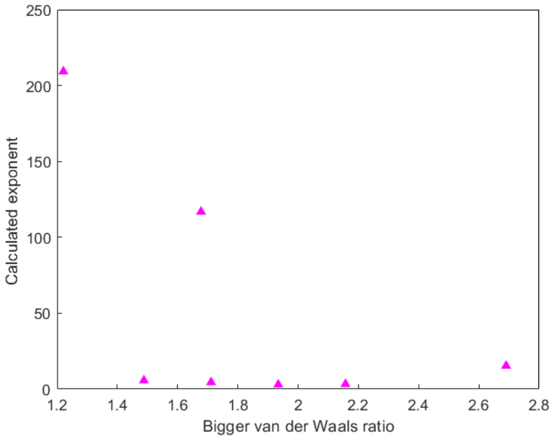

Fig. F.16: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-polyols for the first method.

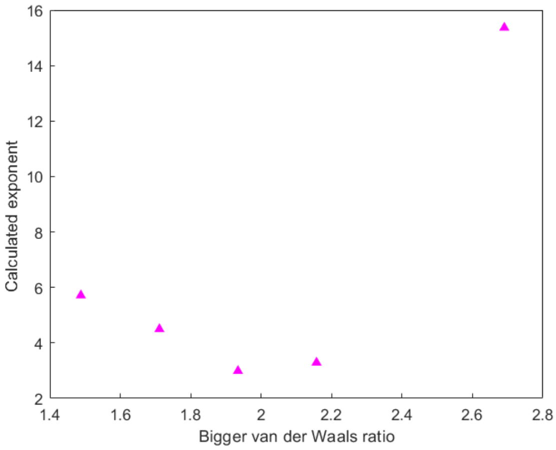

Fig. F.17: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-polyols for the first method without extremely high values ($n > 20$).

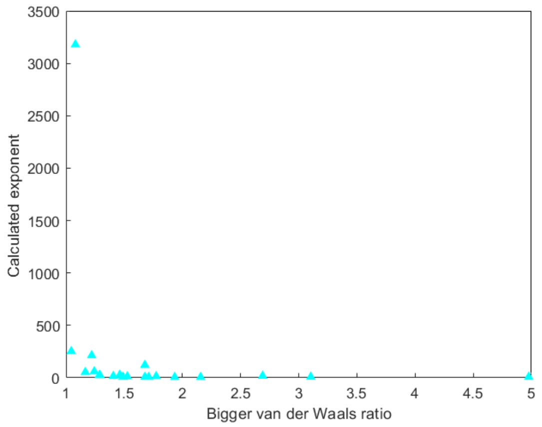

Fig. F.18: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-polyols for the second method.

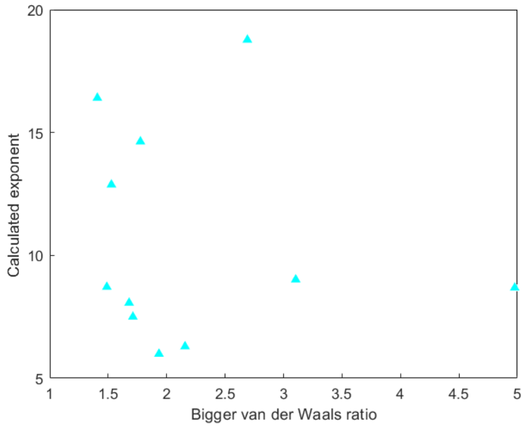

Fig. F.19: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-polyols for the second method without extremely high values ($n > 20$).

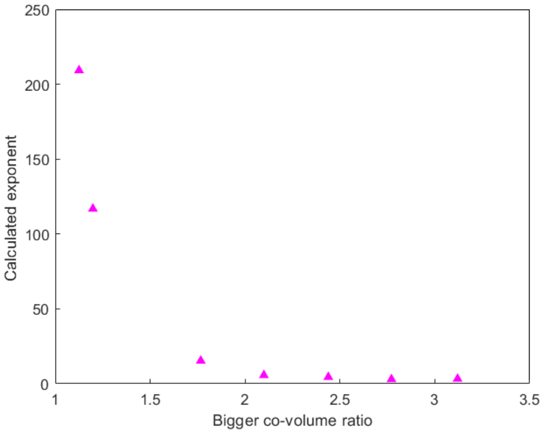

Fig. F.20: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-polyols for the first method.

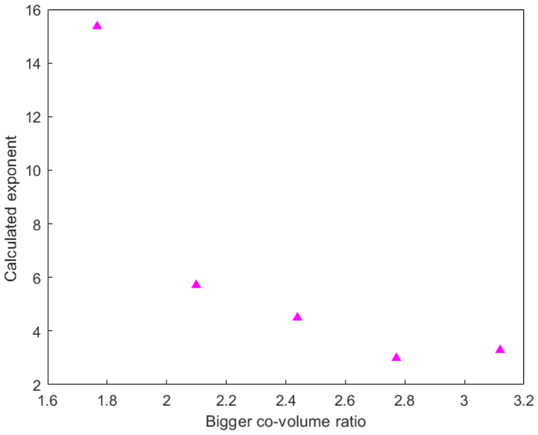

Fig. F.21: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-polyols for the first method without extremely high values ($n > 20$).

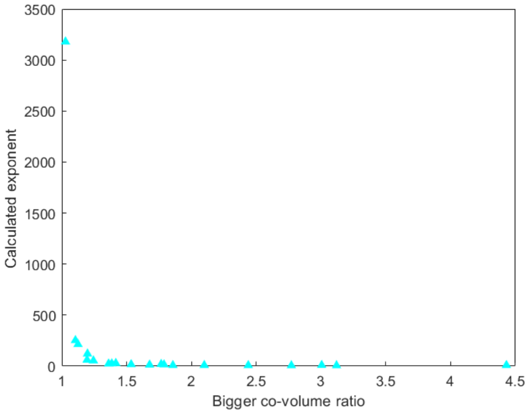

Fig. F.22: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-polyols for the second method.

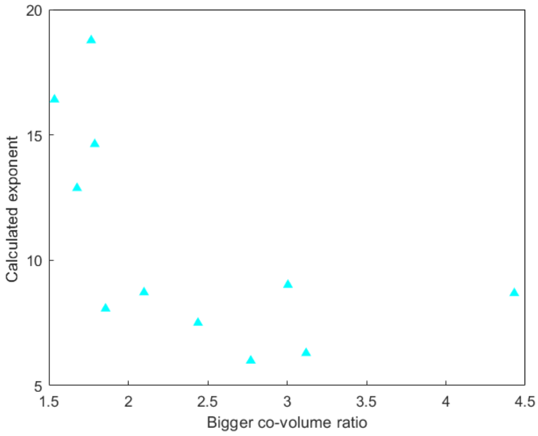

Fig. F.23: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-polyols for the second method without extremely high values ($n > 20$).

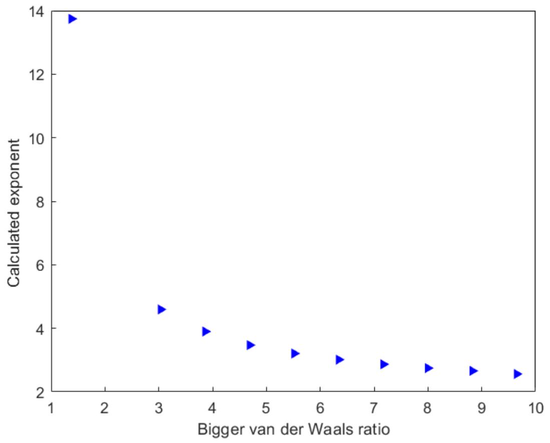

Fig. F.24: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-water for the first method.

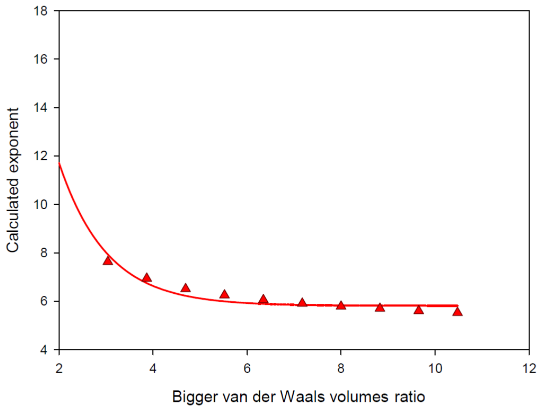

Fig. F.25: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-water for the second method. The regression (–) follows equation $n = 5.82 + 4.25 \cdot 10^1 \cdot e^{-0.987 \cdot V_{\text{ratio}}}$, with a determination coefficient of 0.9957.

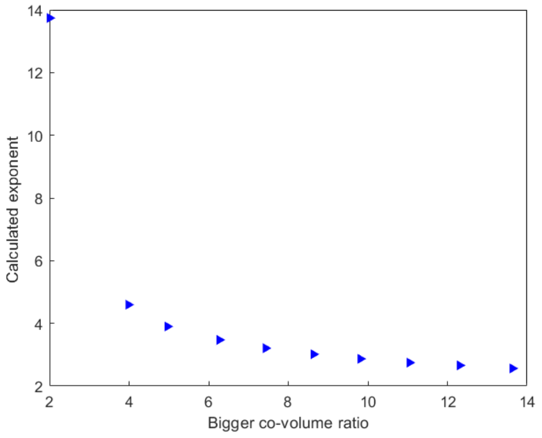

Fig. F.26: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-water for the first method.

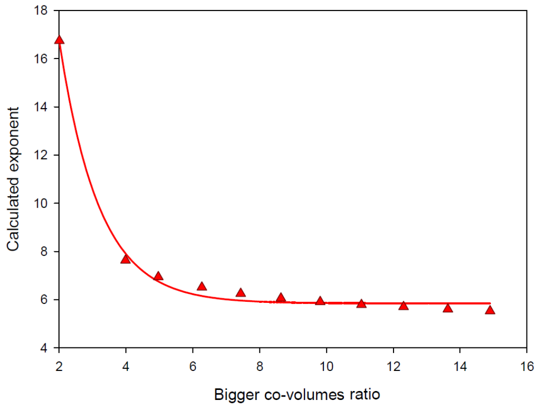

Fig. F.27: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-water for the second method.The regression (–) follows equation $n = 5.85 + 5.83 \cdot 10^1 \cdot e^{-0.838 \cdot b_{\text{ratio}}}$, with a determination coefficient of 0.9948.

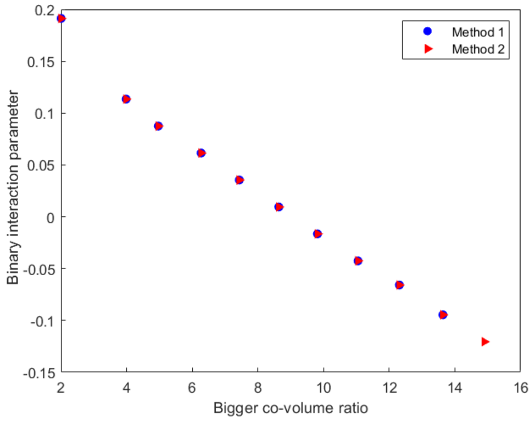

Fig. F.28: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of co-volumes in alkanes-water for both the methods.

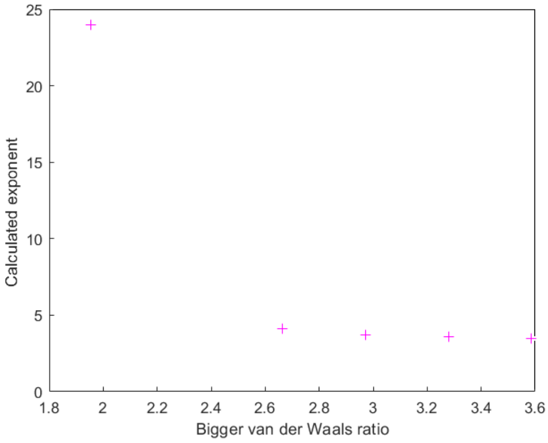

Fig. F.29: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in acetic acid-alkanes for the first method.

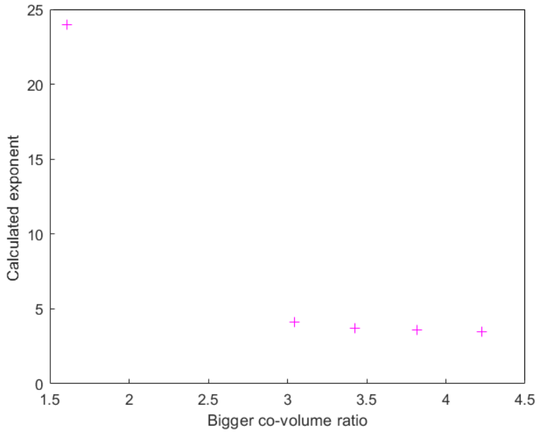

Fig. F.30: Study of dependence of the calculated exponent n with the ratio of co-volumes in acetic acid-alkanes for the first method.

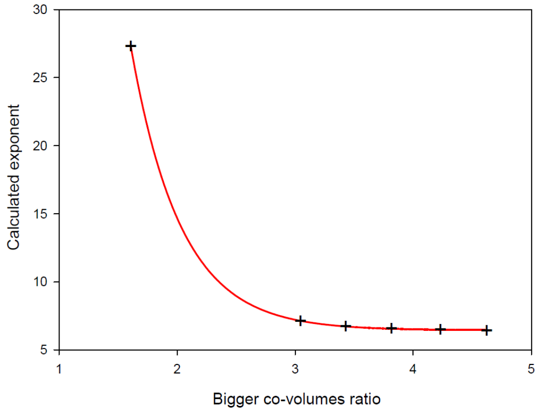

Fig. F.31: Study of dependence of the calculated exponent n with the ratio of co-volumes in acetic acid-alkanes for the second method. The regression (–) follows equation $n = 6.45 + 9.40 \cdot 10^2 \cdot e^{-2.37 \cdot b_{\text{ratio}}}$, with a determination coefficient of 1.0000.

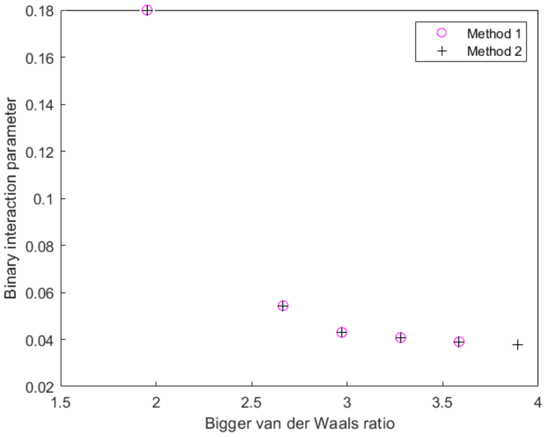

Fig. F.32: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of van der Waals volumes in acetic acid-alkanes for both the methods.

Studies of dependence in binary mixtures

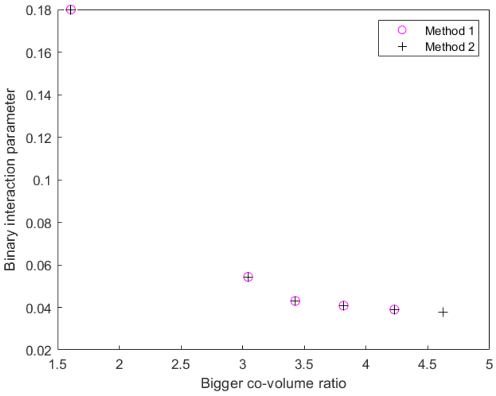

Fig. F.33: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of co-volumes in acetic acid-alkanes for both the methods.

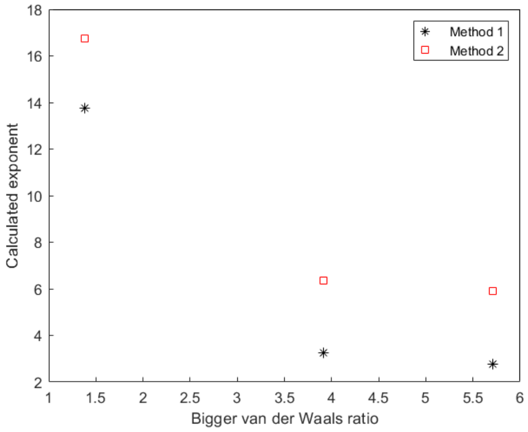

Fig. F.34: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in BTEX-water for both the methods.

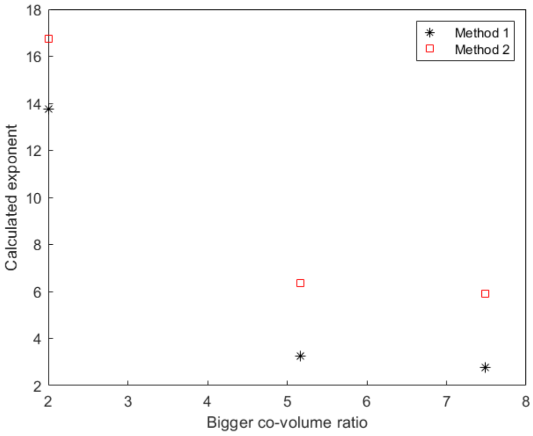

Fig. F.35: Study of dependence of the calculated exponent n with the ratio of co-volumes in BTEX-water for both the methods.

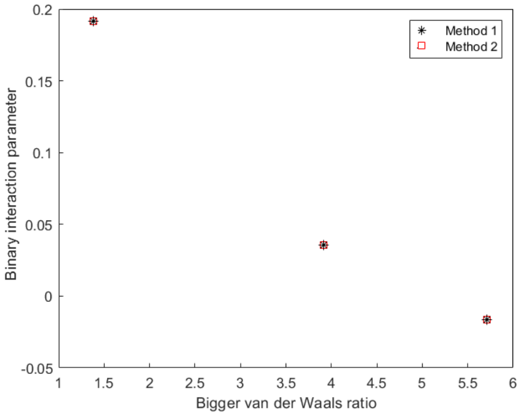

Fig. F.36: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of van der Waals volumes in BTEX-water for both the methods.

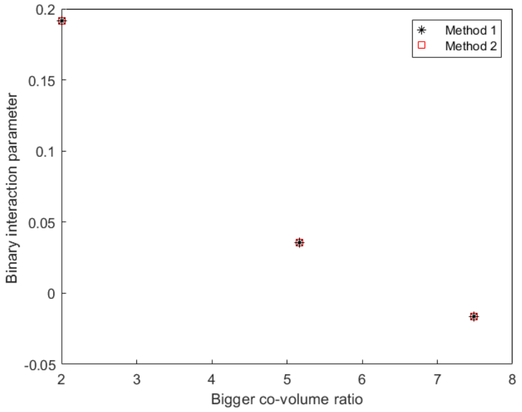

Fig. F.37: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of co-volumes in BTEX-water for both the methods.

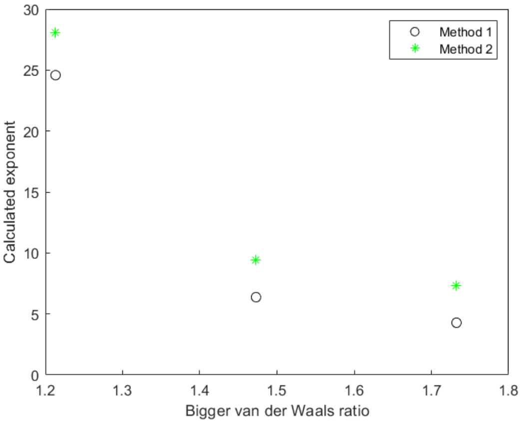

Fig. F.38: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in acetone-hydrocarbons for both the methods.

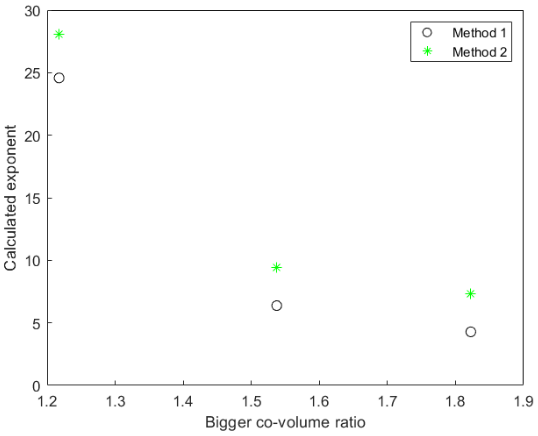

Fig. F.39: Study of dependence of the calculated exponent n with the ratio of co-volumes in acetone-hydrocarbons for both the methods.

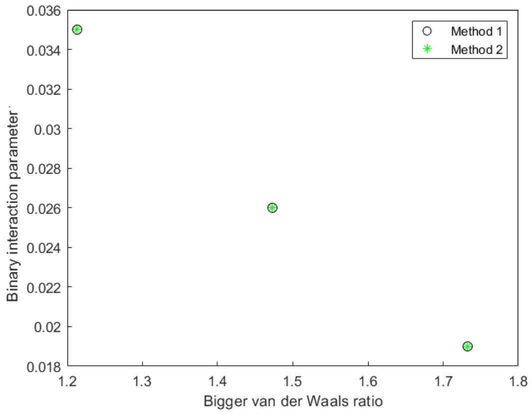

Fig. F.40: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of van der Waals volumes in acetone-hydrocarbons for both the methods.

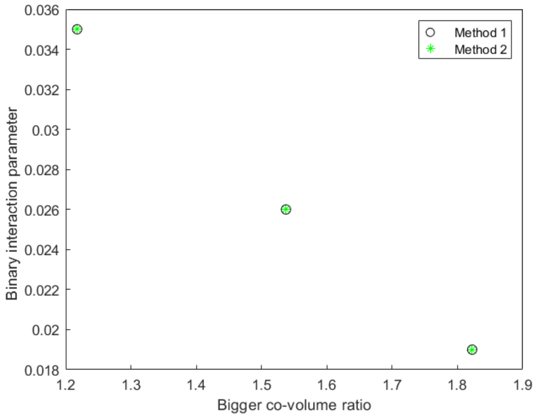

Fig. F.41: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of co-volumes in acetone-hydrocarbons for both the methods.

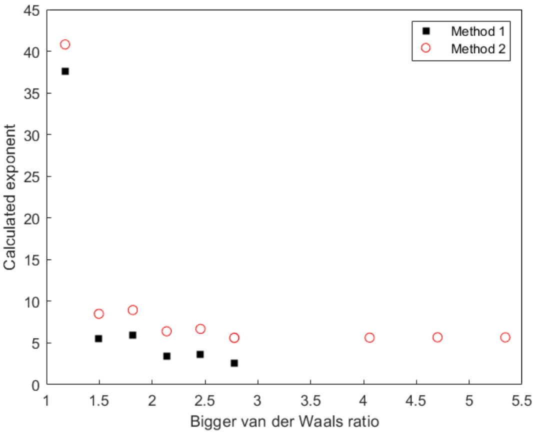

Fig. F.42: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-ethanol for both the methods.

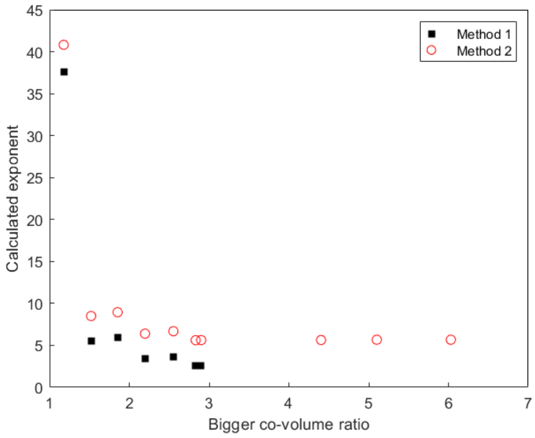

Fig. F.43: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-ethanol for both the methods.

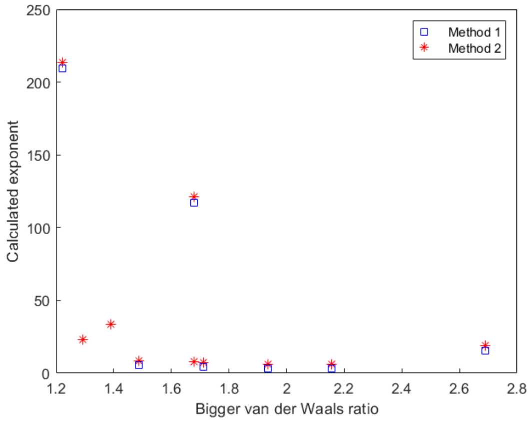

Fig. F.44: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-glycols for both the methods.

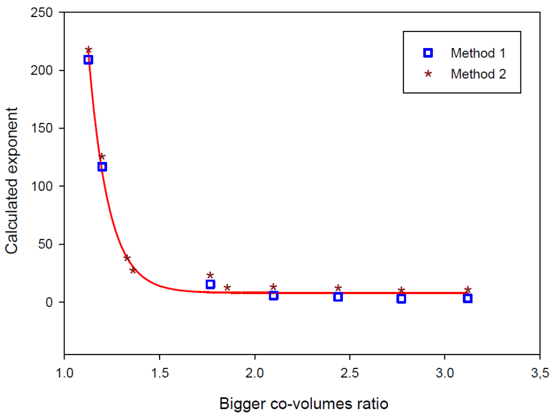

Fig. F.45: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-glycols for both the methods. The regression for the second method (–) follows equation $n = 8.02 + 8.66 \cdot 10^6 \cdot e^{-9.45 \cdot b_{\text{ratio}}}$, with a determination coefficient of 0.9935.

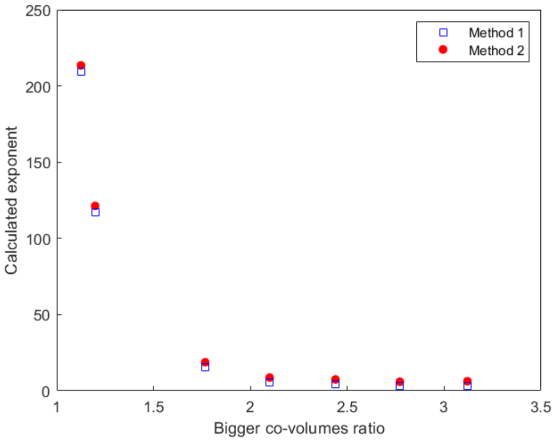

Fig. F.46: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-MEG for both the methods.

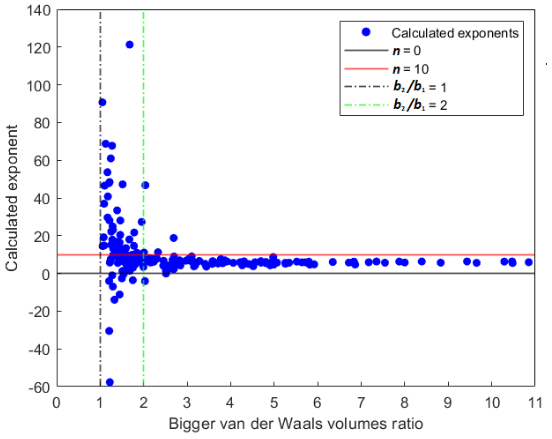

Fig. F.47: Study of dependence of the calculated exponents n with the bigger van der Waals volumes ratio for all the combinations with the second method.

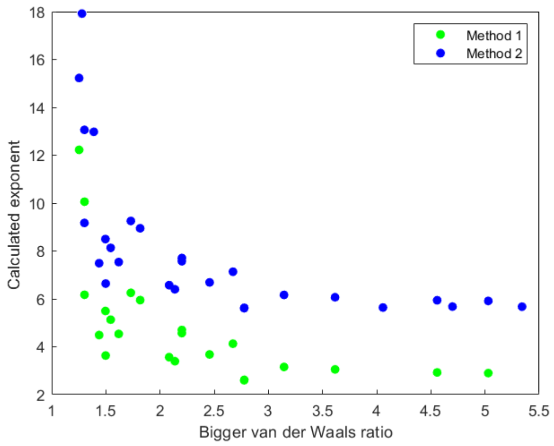

Fig. F.48: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alcohols-alkanes for both the methods without extremely high values ($n > 20$).

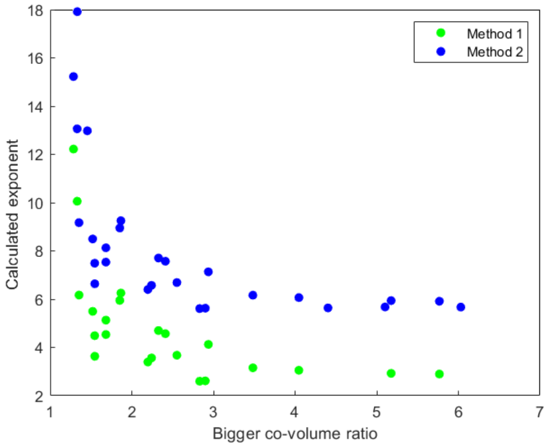

Fig. F.49: Study of dependence of the calculated exponent n with the ratio of co-volumes in alcohols-alkanes for both the methods without extremely high values ($n > 20$).

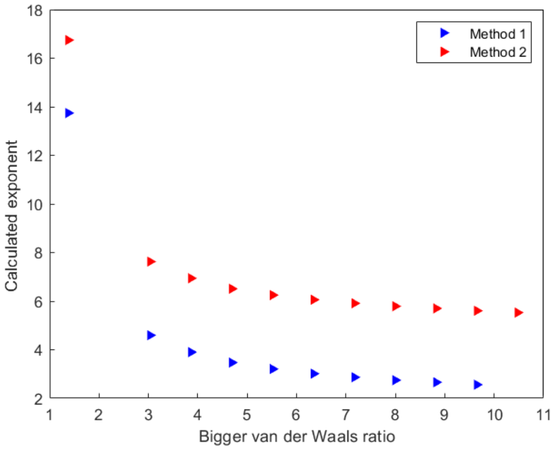

Fig. F.50: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in alkanes-water for both the methods without extremely high values ($n > 20$).

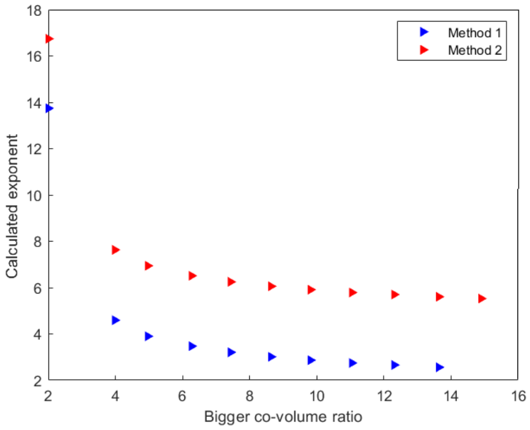

Fig. F.51: Study of dependence of the calculated exponent n with the ratio of co-volumes in alkanes-water for both the methods without extremely high values ($n > 20$).

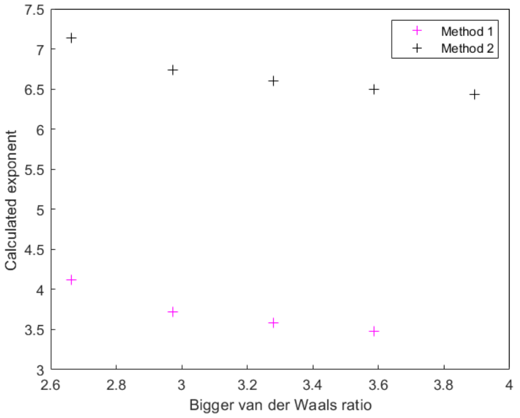

Fig. F.52: Study of dependence of the calculated exponent n with the ratio of van der Waals volumes in acetic acid-alkanes for both the methods without extremely high values ($n > 20$).

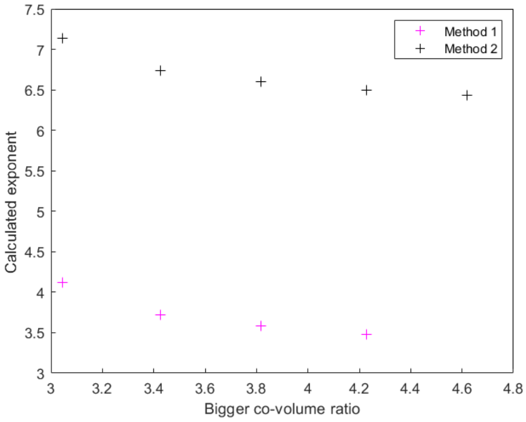

Fig. F.53: Study of dependence of the calculated exponent n with the ratio of co-volumes in acetic acid-alkanes for both the methods without extremely high values ($n > 20$).

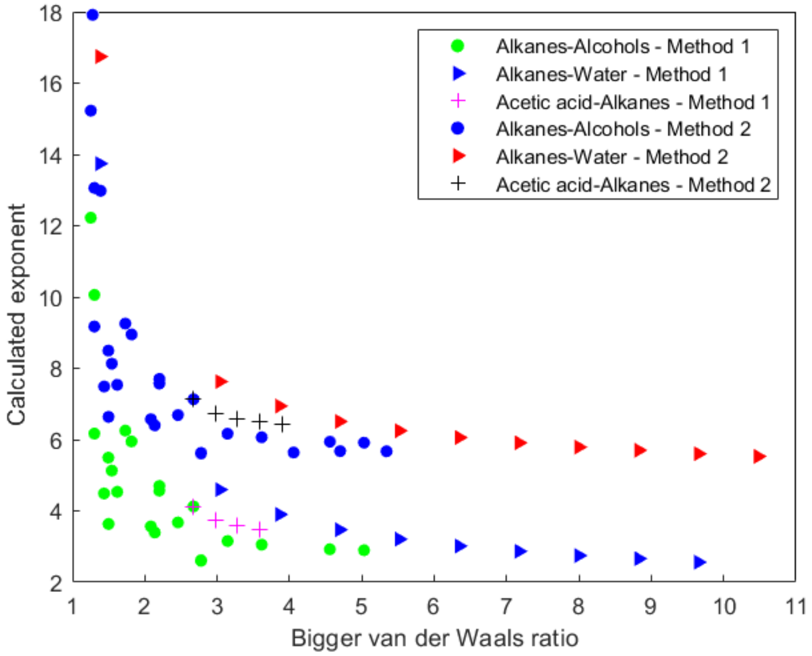

Fig. F.54: Study of dependence of the calculated exponent *n* with the ratio of van der Waals volumes in some different systems for both the methods without extremely high values ($n > 20$).

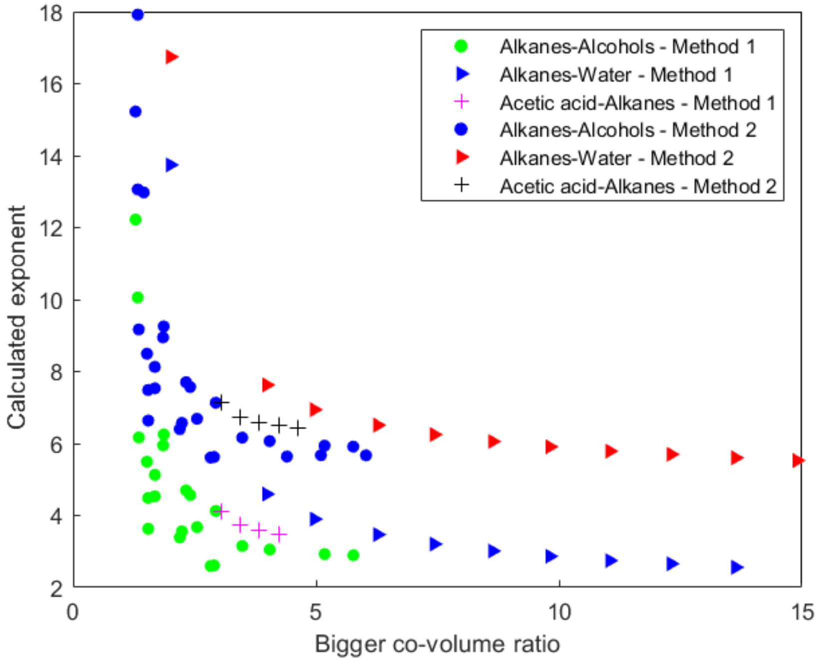

Fig. F.55: Study of dependence of the calculated exponent *n* with the ratio of co-volumes in some different systems for both the methods without extremely high values ($n > 20$).

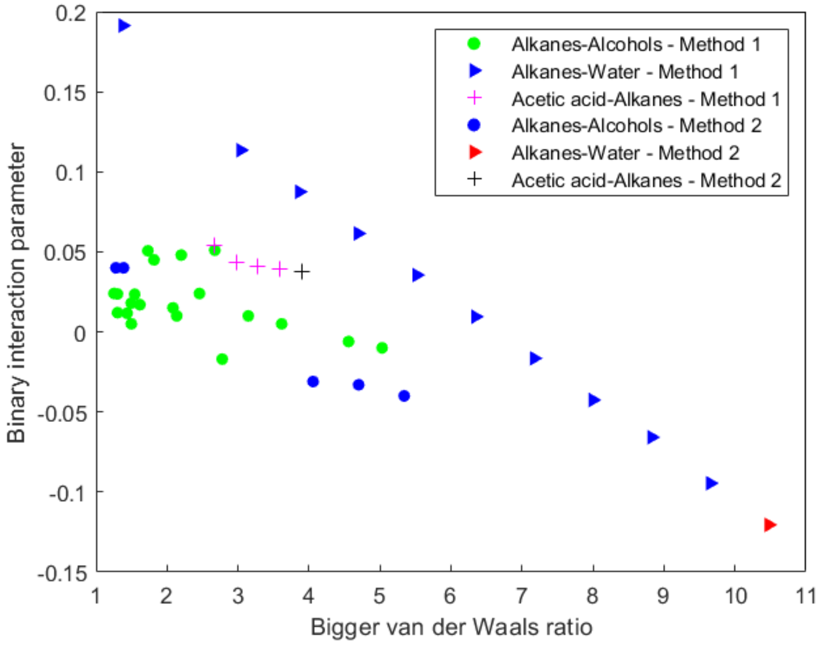

Fig. F.56: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of van der Waals volumes in some different systems for both the methods.

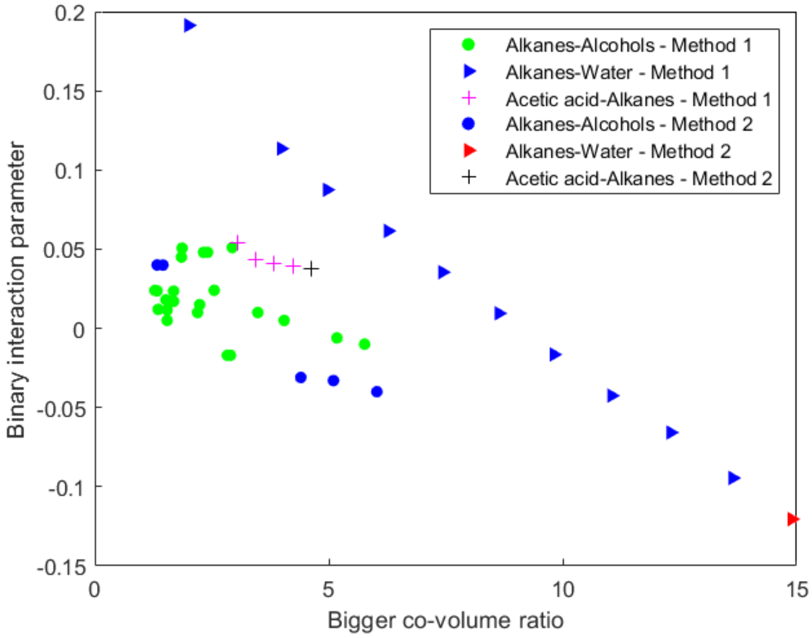

Fig. F.57: Study of dependence of the binary interaction parameter, k_{ij}, with the ratio of co-volumes in some different systems for both the methods.

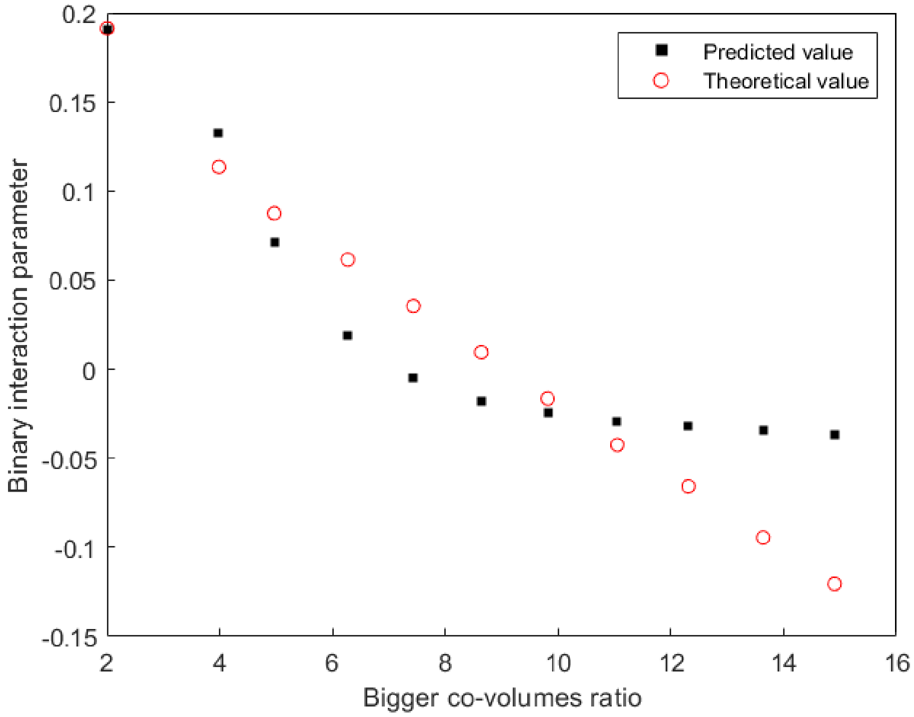

Fig. F.58: Predicted binary interaction parameters, k_{ij}, in acetic alkanes-water for the second method using correlation $n = 5.85 + 5.83 \cdot 10^{1} \cdot e^{-0.838 \cdot b_{\text{ratio}}}$, with a determination coefficient of 0.9948.

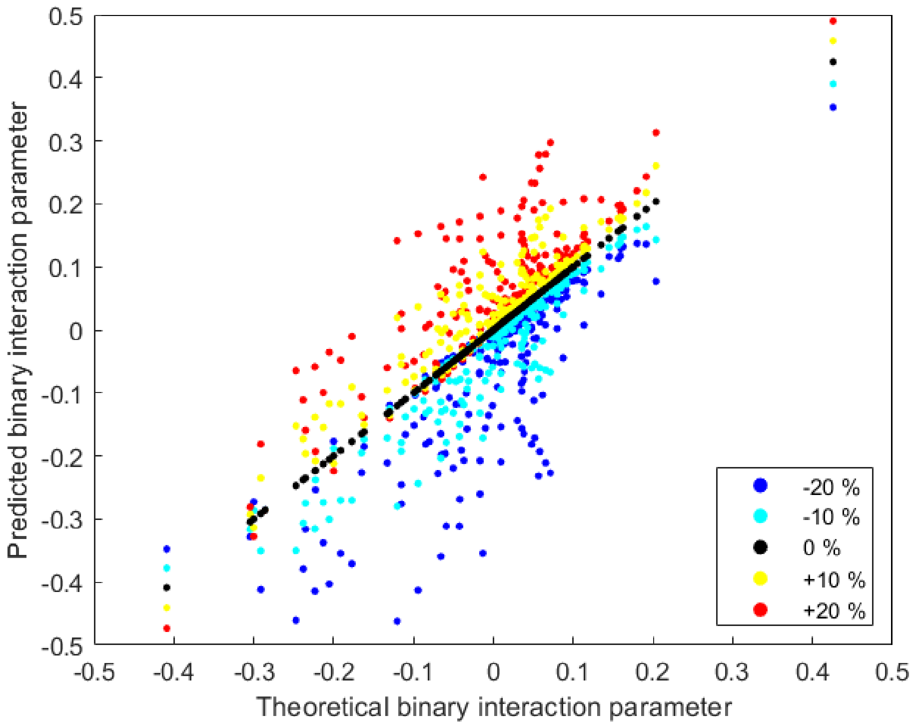

Fig. F.59: Sensitivity analysis for big variations of the exponents n in the determination of the binary interaction parameters, k_{ij}, using the second method.

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Appendix G

MATLAB code

In this appendix, all the MATLAB code written can be observed, firstly, for pure compounds and, lastly, for binary mixtures.

In the pure compounds' section, some of the called functions' content shall not be seen since they were developed in the Center for Energy Resources Engineering [1,2] and their coding structure is not known.

G.1 Pure compounds

```
function CPA_Velho
% First things first
    clc;
    clear all %#ok<*CLALL>
    close all
    format long g
    CHOOSEAMODEL(1) % 1-CPA
    NC_t=185;
    NC=1;
    NOPURECOMP(NC);
    m=410; % Number of columns.
    Step=1; % Step in temperature calculations / K

% Pure compounds' data -------------------------------------------------
MW=[76.09,54.0916,74.12,158.28,140.27,186.34,116.88,102.16,84.16,...
    130.23,112.21,88.1482,60.09,114.23,114.23,74.123,72.11,70.0898,...
    114.18,100.161,74.122,114.23,100.2,86.18,58.12,56.106,93.13,...
    130.231,128.21,86.13,60.1,86.18,128.25,60.052,102.09,58.08,...
    106.124,78.11,122.12,108.14,114.96,79.904,72.11,73.14,134.22,...
    44.01,66.075,61.46,84.16,105.14,74.12,73.14,106.12,102.18,90.08,...
    94.19,46.07,62.13,102.17,102.17,30.07,46.07,106.17,116.16,200.32,...
    228.37,88.11,284.48,130.18,62.13,46.03,172.26,102.13,88.15,256.42,..
    45.08,106.17,112.21,92.09,162.27,80.91,34.1,116.16,117.15,72.11,...
    58.12,74.122,108.14,16.04,32.04,94.94,88.15,102.13,186.24,119.163,..
    214.24,74.08,144.21,270.24,130.18,48.11,100.121,60.05,172.24,298.24,
    158.24,296.5,256.24,116.16,88.11,242.24,228.24,200.24,31.05,98.186,.
    61.08,62.07,106.16,58.12,116.16,144.21,116.16,90.18,102.13,214.31,..
    340.49,158.23,130.18,142.28,310.6,170.33,450.9,282.55,296.6,380.7,..
    100.21,366.7,226.41,86.18,507,123.11,28.01,408.8,268.5,128.2,394.8,.
    254.5,114.23,352.7,212.42,72.15,130.13,102.13,76.16,88.11,116.13,...
    338.7,198.39,422.8,324.6,156.31,108.14,32,106.16,108.14,148.24,...
    94.11,44.1,74.08,120.2,42.08,106.16,79.1,90.08,134.965,166.13,...
    74.12,90.18,194.23,88.1,92.14,119.38,101.19,150.17,18.02];

a0=[13.836,11.7176517818393,15.6949,54.5379516930482,46.5815903645002,..
    71.756,35.73856568,27.178511402827,21.983,41.582,33.63,22.7589,...
    11.9102,32.1660957141895,33.3033,17.31577733,18.1612,18.9939,...
    33.6294,27.9298,18.3137315,34.1842,28.327,21.218440508304,...
    12.9101198526289,12.2366795100879,23.246503,38.4586,39.8656,...
    22.5775,10.6019,23.0442792132632,38.2621205324426,9.1196,...
    23.31410094,7.86473793864429,27.836,17.87699151715,31.822,...
    29.141,19.260947,10.2546396731511,16.6777,16.832281,...
    41.2962916122326,2.6911,6.37788278775593,8.43804,17.3167449861295,..
    20.942,16.4025,17.246,26.408,24.33523498,17.5724,19.6341041430154,..
    8.43541,12.6295827210537,26.3836,26.38364387,5.5092547452125,...
    8.67166,28.86,29.441,70.4,83.11,18.88,104.7,33.187,...
    12.4190385098894,5.37,57.73,23.093,21.76523995,90.7,9.0567,...
    28.8616050986152,32.3264,22.8,55.3253736515302,4.38531429936473,...
    3.8605,28.079,35.614137,16.890366,12.9094,18.31373,...
```

```
    28.4125750886378,2.32037634211438,4.0531,8.57941718957359,21.4505,..
    23.307,59,21.659,74.363,14.5934893,40.53,105.049,34.6,...
    8.23431050317538,22.2695,10.52239108,55.53,122.585,47.06,107,...
    96.06,29.51,18.484,87.973,78.41,66.8,5.4886,26.450466116287,...
    12.139693040266,10.819,29.086,13.14274,29.2373242,40.366,29.237,...
    21.9445901166313,24.015,76.299,138.44,46.66,33.9,47.389,149.4139,...
    62.403,247.5542,129.53,140.3519,196.1025,29.178,186.5301,94.914,...
    23.681,302.3949,32.60544,1.37334321474857,216.9089,119.724,...
    41.250611,205.4853,110.81,34.875,175.5994,85.6417701103819,...
    18.198,34.379,23.626,16.9251020979425,18.975,28.796,166.65,76.618,..
    226.98,155.9231,55.2201,24.9813868153875,1.39,29.2,28.8416006028167,
    48.4176876231215,18.8410451073402,9.11875,13.2676,34.822936502161,..
    8.0700933102504,29.3166287,18.845285,16.960394,15.972215,54.5564,...
    17.1480454999981,20.1114725766097,48.634,18.801411,23.3763020103301,
    15.119,19.502531,39.126,1.2277];

b=[67.5,64.613,79.7,184.41,173.33,221.37,131.33,110.8,102,148.5,137.8,..
    97.455,64.11,139.07,141.199,81.1,77.4,72.8,127.1,109.7,81.05,...
    141.885,124.72,90.4,74.7,69.072,87.74,145.8,144,93,64.11,106.31,...
    157.43,46.8,87.28,59.2,93.2,74.99,101.65,97.3,76.77,42.59,75.8,...
    84.09,144.4,27.3,40.053,41.41,90.38,94.35,82.4,85.7,92.1,115.78,...
    73.1,76.6,49.6,58.9,115.8,115.78,42.9,49.11,108.7,116,215.6,248.6,..
    83.38,317.8,133.2,58.6,30,182.7,99.3,100.34,282.1,53.1,108.72,...
    124.584,70.6,180.22,29.21,29.2,116.31,101.82,76.97,74.7,81.05,...
    97.54,29.1,30.978,43.82,97.9,98.3,202.8,111.45,240.2,66.25,147.3,...
    315.5,131,43.7,92.6,50.06,179.6,351.8,164.6,333.9,278.3,114.7,81.9,.
    278.2,245.5,212.6,36.1,108.71,54.58,51.4,108.72,72.081,118.89,...
    150.6,117.9,92.3,99.4,242.5,410.7,169.2,133.1,178.65,412.09,216.24,.
    620.31,374.384,391.89,514.24,125.35,495.01,296.1,107.89,717.66,...
    98.38,26.05,557.78,353.889,160.35,533.5,333.685,142.44,472.98,...
    274.53,91.008,133.9,99.9,76.2,82.8,116.4,453.35,250.53,577.7,432.47,
    197.909,95.83,21.6,108.6,97.23,161.67,80.1,57.834,64.1,126.85,...
    52.9,109.8,71.58,65.42,68.41,135.01,81.487,93.5,166.581,77.9,...
    92.14,66.5,115.95,128.926,14.515];

Gamma=[2465.453,2181.155,2368.592,3556.97,3232.261,3898.786,3273.13,...
    2950.202,2592.10527203248,3367.992,2935.23918780957,2808.745,...
    2234.515,2781.831,2836.75282366577,2567.95249532649,...
    2822.08069353597,3137.96875588847,3182.28751957766,3062.15412180188,
    2717.777,2897.70909181509,2731.68317398279,2823,2078.622,...
    2130.725,3186.58749736123,3172.50119172672,3329.67357893324,...
    2919.83795469029,1989.06,2607.083,2923.125,2343.797,3212.876,...
    1597.822,3592.16901703316,2867.193,3765.18166917606,3602.11,...
    3017.53240624176,2895.867,2646.26174779118,2407.48986457702,...
    3439.614,1551.222,1915.17,2450.76797439384,2828.913,...
    2669.57482412843,2394.13525516645,2420.458,3448.783,2528.086,...
    2891.20942391617,3082.82,2045.568,2578.93,2740.25729052133,...
    2740.887,1544.548,2123.828,3193.24786071308,3052.53333454325,...
    3927.26086480277,4020.85123522078,2723.517,3962.4029292593,...
```

```
    2996.6058134808,2548.92,2258.6,3800.39604424197,2797.02890382278,...
    2609.032,3866.96328018499,2051.471,3192.838,3120.76394008162,...
    2010.21798161204,3692.217,1805.656,1590.102,2903.549,...
    4206.83210396864,2639.2675683836,2078.5060985577,2717.62566375745,..
    3503.432,959.028,1573.707,2354.785,2635.24243478176,...
    2851.66631473929,3499.04806464029,2337.35229389154,...
    3723.48617942785,2649.496,3309.3271638121,4004.5932057739,...
    3176.65938463102,2266.27,2892.44644681935,2528.212,3718.66613143875,
    4190.90043747878,3438.64972607203,3854.19075961383,4151.40613882833,
    3094.36570286408,2714.42536738836,3803.27846039392,3841.36703056265,
    3779.01877430399,1828.708,2926.373,2675.1,2531.71,3217.841,2193.083,
    2962.065,3223.71463784977,2982.53020001468,2859.51,2905.77547393341,
    3783.7,4054.17727538981,3316.73079404299,3063.28560411527,...
    3190.542,4360.78598489562,3471.038,4799.84666510499,4161.435,...
    4307.44719251016,4586.51821295252,2799.762,4532.11371109291,3855.51,
    2640.03,5067.82452413151,3986.10830205077,634.07,4677.13904627199,..
    4069.154,3094.221,4632.46537864698,3994.222,2944.911,...
    4465.2532775751,3751.99,2405.105,3088.00866424649,2844.39927077057,.
    2671.42,2756.24167464674,2975.3977605671,4421.17336672131,3678.418,.
    4725.5359489737,4336.30999533027,3357.694,3135.313,773.974,...
    3233.84256754133,3567.672,3601.973,2829.035,1896.453,2489.57,...
    3301.724,1834.8,3211.454,3166.48082832249,3118.1086525374,...
    2808.09246618922,4860.1045837261,2531,2587.01,3789.49,...
    2902.81148551448,3051.36,2734.43288884653,2022.95429672501,...
    3622.49,1017.338];

c1=[0.9372,0.69706,0.9784,1.068634,1.0642,0.965,1.01096,0.9805,0.843,...
    1.1486,0.97,0.9358,0.91709,0.87461,0.92763,0.88935,0.8476,0.814,...
    1.021,0.965,0.90354,0.96008,0.8991,0.7561,0.7021,0.71721,0.86376,...
    1.1689,1.0432,0.9127,0.9468,0.79961,0.9439,0.4644,1.03323,0.9951,...
    0.8814,0.7576,1.367,0.7533,0.88853,0.63608,0.8803,0.75803,0.9618,...
    0.7602,0.598077,0.76412,0.74265,1.5743,0.84805,0.8838,0.7991,...
    0.94902,0.8937,0.7992,0.72125,0.7213,0.92963,0.92963,0.58463,...
    0.7369,0.8539,0.9103,1.2163,1.2817,0.94265,1.577,1.0422,0.7221,...
    0.3338,1.1336,1.0334,0.84978,1.4865,0.7382,0.8539,0.82473,1.18,...
    1.0436,0.60051,0.50222,1.03889,0.9411,0.91279,0.7021,0.90354,...
    0.82074,0.44718,0.43102,0.66928,0.88703,0.9974,1.3097,1.3371,1.3768,
    0.87185,1.129,1.5496,1.0853,0.8007,0.91446,0.79622,1.0968,1.5966,...
    1.1552,1.86,1.3268,0.9976,0.967,1.4744,1.3667,1.2451,0.6044,0.77664,
    0.8316,0.6744,0.8681,0.70771,0.97798,1.0704,1.025,0.8916,0.9629,...
    1.1315,1.7166,1.1811,1.1038,1.13243,1.59552,1.19531,1.96495,1.53669,
    1.55978,1.80798,0.9137,1.75615,1.3728,0.8313,1.99279,0.8447,...
    0.49855,1.86409,1.50837,1.04628,1.9331,1.46978,0.99415,1.72818,...
    1.3404,0.79858,1.0333,1.045,0.8398,0.9189,1.0161,1.67916,1.29057,...
    1.89769,1.66798,1.1437,0.896,0.4754,0.88,0.8298,0.9795,0.9087,...
    0.6307,0.6891,0.9117,0.6777,0.86256,0.77061,0.87733,0.75793,1.48450,
    0.96139,0.814,1.59108,0.58312,0.8037,0.74544,0.78212,0.967579,0.6735

omega=zeros(NC_t,1);
```

```
omega=omega+0.5;

epsilon=[2097.907,0,2525.86,3013.52,0,4064.349,3159.971,2525.86,0,...
    3218.547,0,2525.86,2525.86,0,0,2525.98027423623,0,0,0,0,2749.82,0,..
    0,0,0,0,0,2480.85786746631,0,0,2525.86,0,0,4850.012,0,1343.878,0,0,.
    2049.92201934822,2470.512,0,0,0,1414.55083029916,0,0,0,0,...
    0,1943.48098513541,0,445.129,2367.573,0,0,0,0,0,0,0,0,...
    2589.848,0,0,0,0,0,0,0,0,5041.5,0,0,0,0,1120.7,0,0,...
    1688.1427753797,0,0,654.271,0,0,1319.36247762415,0,...
    2749.6665809868,2406.543,0,2957.782,0,0,0,0,1943.48098513541,0,...
    0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1379.12,0,1970,2375.752,0,0,...
    1136.036,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,...
    0,0,0,0,0,0,0,0,0,0,0,0,0,1966.322,0,0,2490.137,0,2103.44,0,...
    4808.155,0,0,0,1604.0976563994,0,0,2049.92201934822,2572.22,0,...
    1140.83,1471.43604606372,0,0,1581.52494080498,1697.13,2003.248];

beta=[19,0,8.2,0.364,0,0.12,0.3,3.3,0,0.14,0,3.6,8.1,0,0,2.2,0,0,0,0,...
    1,0,0,0,0,0,0,1.07,0,0,9.1,0,0,4.5,0,289,0,0,1.2,2.4,0,0,0,33.8039,.
    0,0,0,0,0,33.2,0,110.8,6.4,0,0,0,0,0,0,0,0,8,0,0,0,0,0,0,0,0,...
    15.5,0,0,0,0,43,0,0,25,0,0,58.32,0,0,0.509004,0,1,6.7,0,16.1,0,...
    0,0,0,33.2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,33.7,0,13,14.1,0,0,..
    5.9,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,..
    0,0,0,0,0,0,0,0,0,0,26.7,0,0,4.1,0,45.3,0,2.1,0,0,0,0.6933,0,0,1.2,.
    0.961,0,34.343,46.51,0,0,77.2426,19.8422,69.2];

scheme=[22,0,11,12,0,11,11,11,0,11,0,11,11,0,0,11,0,0,0,0,11,0,0,0,0,0,.
    0,11,0,0,11,0,0,100,0,11,0,0,11,12,0,0,0,11,0,0,0,0,0,22,0,11,22,...
    0,0,0,0,0,0,0,0,11,0,0,0,0,0,0,0,0,100,0,0,0,0,11,0,0,22,0,0,12,0,..
    0,11,0,11,11,0,11,0,0,0,0,22,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,11,
    0,22,22,0,0,11,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,.
    0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,11,0,0,11,0,11,0,100,0,0,0,11,0,0,111,
    11,0,22,11,0,0,11,22,22];

Tc=[626,425.17,563.05,687,616.4,719.4,631.9,611.35,504.03,652.5,566.6,..
    586.15,536.78,543.96,553.5,536.05,535.5,565,611.4,587.61,547.78,...
    559.64,530.37,497.7,408.14,417.9,622,629.8,632.7,561.05,508.3,...
    504.43,590.15,591.95,606,508.2,695,562.16,751,720.15,579,584.15,...
    537.2,524,660.55,304.21,378.8,566.73,536.05,736.6,466.7,496.6,...
    744.6,500.05,557,615.02,400.1,503.04,530.6,530.6,305.32,513.92,...
    617.2,571,649.6,705.9,523.3,795.5,587.9,499.15,588,593.8,546,500.23,
    763.4,456.15,617.2,609.15,766.1,698,363.15,373.53,560.8,516.85,513,.
    408.14,547.78,705.85,190.56,512.64,467,512.74,554.5,686.9,741.9,...
    712,506.55,612.3,762.2,590.5,469.95,566,487.2,655.7,781.1,634.1,764,
    786.5,566.9,530.6,471.2,742.9,699.3,430.05,572.19,671.4,720,617.05,.
    425.18,563.8,616,563.8,570.1,559,674,764,629,594.6,617.7,787,658,...
    855,768,778,826,540.2,819,723,507.6,874,720,126.2,838,758,594.6,832,
    747,568.7,812,708,469.7,593.7,549.7,536.6,538,568.6,804,693,844,796,
    639,697.55,154.58,630.3,704.65,679.9,694.25,369.83,600.81,638.38,...
    364.9,616.23,619,585,542.15,883.6,506.2,530.01,795,632,591.8,536.4,.
```

```
    535.35,769.5,647.29];

    Tc_2=Tc; % Vector saving all critical temperatures without changes.

    % These critical temperatures were terribly wrong.
    Tc(48)=449;
    Tc(84)=790;
    Tc(111)=741.2;
    Tc(79)=850;

Pc=[5.941,4.32,4.414,2.308,2.223,1.954,3.085,3.446,3.21,2.783,2.663,...
    3.897,5.169,2.57,2.56,4.1885,4.207,3.87,2.97,3.3,4.295,2.5,2.74,...
    3.04,3.64,4.0,4.6,2.749,2.709,3.672,4.765,3.12,2.34,5.786,4.0,...
    4.7,4.65,4.895,4.47,4.374,4.58,10.3,4.41,4.2,2.89,7.383,6.349,...
    5.99,4.08,4.27,3.64,3.71,4.6,2.88,4.5,5.36,5.6336,5.53,3.028,3.028..
    4.872,6.137,3.609,2.95,1.788,1.529,3.88,1.156,2.84,5.49,5.81,2.118,.
    3.362,3.37007,1.323,5.62,3.609,3.04,7.5,2.38,8.552,8.96291,3.01,...
    4.3,4.21,3.64,4.295,4.56,4.599,8.084,6.929,3.371,3.473,1.942,4.16,..
    1.65,4.75,0,1.235,0,7.23,3.68,6.0,0,1.084,2.384,1.28,0,0,4.004,...
    1.421,0,0,7.46,3.48,7.124,8.2,3.541,3.796,3.09,0,3.09,3.97,3.51,...
    1.74,1.11,2.33,2.80,2.11,1.06,1.82,0.75,1.16,1.11,0.883,2.74,0.91,..
    1.40,3.025,0.68,4.40,3.40,0.826,1.21,2.29,0.85,1.27,2.49,0.95,1.48,.
    3.37,0,3.36,4.63,4.02,3.06,0.98,1.57,0.80,1.02,1.95,5.01,5.043,...
    3.732,5.15,2.604,6.13,4.248,4.668,3.200,4.60,3.511,5.63,5.82,...
    4.61,3.486,3.972,4.06,2.59,5.16,4.108,5.472,3.04,3.32,22.064];
    % From DIADEM Professional.

Pc2=Pc*1000000;

%DIPPR correlations' parameters
A_1=[1.015,1.2346,0.98279,0.38208,0.43901,0.30207,0.55687,0.70093,...
    0.76925,0.48979,0.55499,0.81754,1.2457,0.59059,0.5903,0.97552,...
    0.94835,0.82381,0.58294,0.68716,0.98965,0.52942,0.63993,0.72701,...
    1.0631,1.1446,0.70358,0.52497,0.50091,0.79424,1.1799,0.72752,...
    0.51244,1.4486,0.79388,1.1931,0.79368,1.0259,0.71587,0.59867,...
    0.9514,2.1872,1.03387,0.80533,0.50812,2.768,1.9688,1.4095,0.88998,..
    0.68184,0.9554,0.85379,0.83692,0.69213,1.0346,1.1058,1.5693,1.4029,.
    0.7239,0.7239,1.9122,1.6288,0.70041,0.63566,0.31252,0.25673,0.8996,.
    0.18308,0.60008,1.3047,1.938,0.39251,0.7405,0.7908,0.21541,1.0936,..
    0.70041,0.61587,0.92382,0.4405,2.832,2.7672,0.68982,0.4993,0.97562,.
    1.0631,0.98965,0.9061,2.9214,2.3267,1.796,0.8363,0.76983,0.34003,...
    0.67439,0.27872,1.13,0,0.19488,0,1.9323,0.7761,1.525,0,...
    0.16691,0.44065,0.24755,0.000,0.000,0.9147,0.23058,0,0.000,...
    1.39,0.73109,1.0011,1.3717,0.68902,1.0677,0.67794,0,0.67794,...
    0.89458,0.79185,0.3105,0.20944,0.48713,0.5981,0.41084,0.16199,...
    0.33267,0.1055,0.18166,0.1716,0.12857,0.61259,0.13364,0.23289,...
    0.70824,0.093576,0.69123,3.2091,0.11855,0.19199,0.46321,0.12287,...
    0.20448,0.5266,0.14071,0.25142,0.84947,0,0.73041,1.0714,...
    0.915,0.6761,0.1466,0.27248,0.114,0.15412,0.36703,0.95937,3.9143,...
```

```
    0.69962,1.1503,0.46833,1.3798,1.3757,1.0969,0.57233,1.4403,0.67752,.
    0.9815,1.159,1.1255,0.41922,0.92128,0.89717,0.46246,1.1628,0.8792,..
    1.0841,0.7035,0.59672,0];

B_1=[0.25071,0.27216,0.2683,0.24645,0.25661,0.23789,0.24725,0.26776,...
    0.26809,0.24931,0.25952,0.26732,0.27281,0.27424,0.2728,0.26339,...
    0.25321,0.22952,0.25416,0.25906,0.27129,0.26034,0.2695,0.26754,...
    0.27506,0.2724,0.2357,0.26186,0.24895,0.25495,0.2644,0.26773,...
    0.26801,0.25892,0.24119,0.25414,0.25711,0.26666,0.24812,0.22849,...
    0.2541,0.29527,0.266739,0.24965,0.25238,0.26212,0.26599,0.22974,...
    0.27376,0.23796,0.26847,0.25675,0.26112,0.26974,0.25968,0.27866,...
    0.2679,0.27991,0.27653,0.27653,0.27937,0.27469,0.26162,0.25613,...
    0.24267,0.23582,0.25856,0.22334,0.26524,0.2694,0.24225,0.25033,...
    0.25563,0.266,0.22958,0.22636,0.26162,0.26477,0.24386,0.26114,...
    0.2832,0.27369,0.26832,0.2125,0.25785,0.27506,0.27129,0.28268,...
    0.28976,0.27073,0.27065,0.27514,0.26173,0.24293,0.25541,0.23697,...
    0.2593,0,0.22321,0,0.28018,0.25068,0.2634,0,0.21846,0.25169,...
    0.2624,0,0,0.2594,0.22874,0,0,0.21405,0.26971,0.22523,0.25663,...
    0.26086,0.27188,0.2637,0,0.2637,0.27463,0.26606,0.25143,...
    0.25761,0.26646,0.26518,0.25175,0.22994,0.24664,0.22289,0.23351,...
    0.23153,0.22647,0.26211,0.22674,0.23659,0.26411,0.22289,0.24124,...
    0.2861,0.22525,0.23337,0.25444,0.22561,0.23474,0.25693,0.22812,...
    0.23837,0.26726,0.000,0.25456,0.27214,0.26134,0.26304,0.22839,...
    0.24007,0.22422,0.22928,0.24876,0.2882,0.28772,0.26143,0.31861,...
    0.25746,0.31598,0.27453,0.25568,0.25171,0.26852,0.25887,0.24957,...
    0.25943,0.26336,0.17775,0.25442,0.27544,0.26085,0.28954,0.27136,...
    0.2581,0.27386,0.26217,0];

C_1=[626.14,425.00,563.10,688.00,616.60,718.70,632.30,610,504.00,...
    652.30,566.90,588.1,536.80,543.80,553.50,535.90,536.70,565.00,...
    611.40,587.10,547.80,559.70,530.40,497.7,407.80,417.90,621.00,...
    629.80,632.70,561.19,508.30,504.60,587.65,591.95,606.00,508.10,...
    695.00,562.05,751.00,720.15,579.00,584.15,537.20,531.90,660.50,...
    304.21,378.80,449.00,553.80,736.60,466.70,496.60,744.6,500.05,...
    548.00,615.00,400.10,503.04,530.6,530.6,305.32,514.00,617.15,...
    571.00,688.10,716.30,523.30,759.40,587.95,499.15,588.00,649.00,...
    546.00,500.23,738.70,456.15,617.15,609.15,850.00,698.15,363.15,...
    373.53,560.80,790.00,519.00,407.80,547.80,705.85,190.56,512.50,...
    464.00,512.74,554.50,686.90,741.90,712.00,506.55,00,762.20,...
    0.000,469.95,566.00,487.20,0.000,781.10,650.70,764.00,0.000,0.000,..
    530.60,741.20,0.000,0.000,430.05,572.10,678.20,719.00,617.00,...
    425.12,575.40,0.00,575.40,570.10,559.00,674,764.00,629.00,...
    594.60,617.17,787.00,658.00,855.00,768.00,778.00,826.00,540.20,...
    819.00,723.00,507.06,874.00,719.00,126.20,838.00,758.00,594.60,...
    832.00,747.00,568.70,812.00,708.00,469.70,0,549.73,536.60,...
    538.00,568.60,804.00,693.00,844.00,796.00,639.00,697.55,154.58,...
    630.3,704.65,679.90,694.25,369.83,600.81,638.35,364.85,616.20,...
    619.95,604.00,545.00,883.60,506.20,530.00,795.00,631.95,591.75,...
    536.4,535.15,769.50,647.096];
```

```
D_1=[0.23083,0.28707,0.25488,0.26125,0.29148,0.264,0.31471,0.24919,...
    0.28571,0.27824,0.28571,0.25348,0.23994,0.2847,0.2985,0.26864,...
    0.28974,0.255,0.28698,0.27421,0.23809,0.27027,0.2793,0.28268,...
    0.2758,0.28172,.26124,0.25257,0.29781,0.29069,0.24653,0.26799,...
    0.29044,0.2529,0.29817,0.292,0.28673,0.28394,0.2857,0.23567,...
    0.2857,0.3295,0.28571,0.24306,0.29373,0.2908,0.3433,0.2386,...
    0.28571,0.2062,0.2814,0.27027,0.2422,0.28571,0.27542,0.31082,...
    0.2882,0.2741,0.2794,0.2794,0.29187,0.23178,0.28454,0.27829,...
    0.28571,0.28571,0.278,0.28291,0.30068,0.27866,0.24435,0.28571,...
    0.2795,0.292,0.28571,0.25522,0.28454,0.28054,0.22114,0.29621,...
    0.28571,0.29015,0.27599,0.2324,0.28571,0.2758,0.23809,0.2707,...
    0.28881,0.24713,0.28947,0.27553,0.26879,0.28571,0.26326,0.28571,...
    0.2764,0,.2975,0,0.28523,0.29773,0.2806,0,0.28435,0.30033,...
    0.33247,0,0,0.2774,0.30337,0.0,0.0,0.2275,0.29185,0.21515,0.22173,..
    0.27479,0.28688,0.29318,0,0.29318,0.28512,0.2785,0.28571,...
    0.37571,0.2965,0.28571,0.28571,0.28571,0.28571,0.28571,0.28571,...
    0.28571,0.28571,0.28141,0.28571,0.28571,0.27537,0.28571,0.28135,...
    0.2966,0.28571,0.28571,0.28571,0.28571,0.28571,0.28571,0.28571,...
    0.28571,0.27789,0.00,0.27666,0.29481,0.28,0.28901,0.28571,...
    0.28571,0.28571,0.28571,0.28571,0.2857,0.2924,0.27365,0.30104,...
    0.2813,0.32768,0.29359,0.26857,0.29616,0.28775,0.27596,0.29295,...
    0.2857,0.29557,0.28571,0.27586,0.31364,0.27179,0.28674,0.29241,...
    0.2741,0.2872,0.24631,0];

A_2=[135.491,75.572,106.29483,156.23933,68.401,186.98632,147.41,...
    135.42149,51.9766,144.110183,74.936,114.74801,84.66416,84.912,134.5,
    122.552,84.5303,80.0555,105.753,97.6746,121.78,90.847,59.531,53.579,
    108.43,78.01,91.273,185.828,111.918,91.2588,110.717,57.09,74.254,...
    53.27,67.1818,57.9764,116.280,83.107,88.513,100.68,61.048,108.26,...
    51.648,65.67,101.22,47.0169,46.8783,31.816,51.087,106.38,136.9,...
    49.314,142.45,41.631,58.033,81.045,44.704,84.39,65.935,65.935,...
    51.857,73.304,89.063,57.661,115.525,131.128,66.824,118.986,54.702,..
    65.551,43.8066,86.9901,105.64,86.898,132.557,81.56,89.063,80.208,...
    99.986,89.03,29.315,85.584,72.31,69.604,65.6601,108.43,121.78,...
    95.403,39.205,82.718,44.7643,60.164,71.87,92.8907,93.829,103.915,...
    61.267,0,110.985,0.0000,54.15,107.36,77.184,0.0000,113.116,...
    74.1777,187.49,0.0000,0.0000,70.717,103.995,0.000,0.00000,75.206,...
    92.684,92.624,91.594,85.099,66.343,122.82,0,122.82,65.382,...
    115.54,279.65,204.71,66.301,71.228,112.73,154.31,137.47,399.52,...
    203.66,140.79,155.76,87.829,155.64,156.06,104.65,574.98,85.828,...
    58.282,208.56,182.54,109.35,292.12,157.68,96.084,159.15,135.57,...
    78.741,0,115.16,62.165,104.08,78.318,211.42,140.47,386.27,...
    219.83,131.00,210.88,51.245,90.405,118.53,87.938,95.444,59.078,...
    54.552,91.379,43.905,88.72,82.154,63.83,54.571,124.004,172.27,...
    57.518,132.72,75.881,76.945,146.43,56.55,152.48,73.649];

B_2=[-12483.3,-4621.9,-9866.35511,-15212.33492,-7776.9,-17926.83044,...
    -13466,-12288.40621,-5104.66,-13667.15667,-7155.9,-10643.3,...
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    -8307.24422,-6722.2,-8341.1,-10236.2,-6797.16,-7159.76,-9225.3,...
    -8335.14,-10504,-7475.7,-5826.4,-5041.2,-5039.9,-4634.1,-7841.2,...
    -14520.2,-10026.5,-7515.68,-9040,-5239.7,-7515.6,-6304.5,-7463.47,..
    -5355.27,-9331.2,-6486.2,-11829,-11059,-6398.4,-6592,-5301.36,...
    -6168.5,-9255.4,-2839,-3170.5,-3659.4,-5226.4,-13714,-6954.3,...
    -4949,-15050,-4668.7,-5991.3,-6941.3,-3525.6,-5740.6,-6198.5,...
    -6198.5,-2598.7,-7122.3,-7733.7,-6346.5,-12592.2,-14521.5,-6227.6,..
    -15352.6,-6598.8,-5027.4,-5131.03,-9863.35,-8007,-6646.4,-15281.6,..
    -5596.9,-7733.7,-7203.2,-13808,-10020,-2424.5,-3839.3,-6944.3,...
    -9531.2,-5831.52,-5039.9,-10504,-10581,-1324.4,-6904.5,-3907.8,...
    -5621.7,-6885.7,-10794.4,-11727,-12284.5,-5618.6,0,-14440.4,...
    0,-4337.7,-8085.3,-5606.1,0,-15371.6,-8867.22,-19153,0,0,-6439.7,...
    -13179.4,0,0,-5082.8,-7080.8,-10367,-10811,-7615.9,-4363.2,...
    -9253.3,0,-9253.2,-6262.4,-7907,-18664,-19963,-8259.6,-7709.8,...
    -9749.6,-18406,-11976,-36347,-19441,-17129,-20612,-6996.4,-20116,...
    -15015,-6995.5,-48715,-9493.8,-1084.1,-24971,-17897,-9030.4,-28200,.
    -16093,-7900.2,-19976,-13478,-5420.3,0,-8433.9,-5624,-7535.9,...
    -7256.9,-21711,-13231,-34581,-21841,-11143,-13928,-1200.2,-7955.2,..
    -11957,-9496.6,-10113,-3492.6,-7149.4,-8276.8,-3097.8,-7741.2,...
    -7211.3,-6838.3,-5380.3,-17894.4,-11589,-5296.6,-16634,-6910.6,...
    -6729.8,-7792.3,-5681.9,-16449,-7258.2];

C_2=[-16.0191,-8.5323,-11.6553,-18.42393,-6.4637,-22.64004,-17.353,...
    -15.73191,-4.34844,-16.82611,-7.5843,-12.85754,-8.57673,-9.5157,...
    -18.225,-14.125,-9.23358,-8.35479,-12.0698,-10.9872,-13.921,...
    -10.262,-5.4269,-4.6404,-15.012,-8.9575,-10.216,-23.6236,-12.8713,..
    -10.1481,-12.676,-5.1592,-7.4138,-4.2985,-6.24388,-5.21058,...
    -14.639,-9.2194,-8.6826,-10.709,-5.4972,-14.16,-4.2559,-6.2426,...
    -11.538,-3.86388,-3.91038,-1.324,-4.2278,-11.06,-19.254,-3.9256,...
    -16.318,-2.8551,-5.0971,-8.777,-3.4444,-9.6454,-6.3423,-6.3423,...
    -5.1283,-7.1424,-9.917,-5.032,-12.7545,-14.7819,-6.41,-12.8203,...
    -4.4931,-6.6853,-3.18777,-8.90265,-12.477,-9.5758,-14.8904,...
    -9.0779,-9.917,-8.6023,-10.088,-9.2577,-1.1354,-11.199,-7.298,...
    -6.3814,-6.33452,-15.012,-13.921,-10.004,-3.4366,-8.8622,-3.4016,...
    -5.53,-7.0944,-9.6454,-9.56548,-11.0821,-5.6473,0,-11.7854,...
    0,-4.8127,-12.72,-8.392,0.000,-11.9611,-7.10392,-22.989,0,0,-6.9845,
    -10.935,0,0,-8.0919,-10.695,-9.4699,-9.2821,-9.3072,-7.046,...
    -14.99,0,-14.99,-6.2585,-14.945,-38.205,-25.566,-6.0092,...
    -6.8418,-13.245,-17.694,-16.698,-52.626,-25.525,-15.87,-17.548,...
    -9.8802,-17.616,-18.941,-12.702,-77.445,-8.8595,-8.3144,-24.748,...
    -22.498,-12.882,-37.544,-18.954,-11.003,-18.161,-16.022,-8.8253,...
    0,-13.934,-5.8595,-12.348,-8.228,-26.255,-16.859,-50.953,...
    -27.531,-15.855,-29.483,-6.4361,-10.086,-13.293,-9.1808,-10.09,...
    -6.0669,-4.2769,-10.176,-3.4425,-9.8693,-8.8646,-5.8194,-4.6858,...
    -13.156,-22.113,-5.2078,-14.643,-7.9499,-8.179,-20.614,-4.9815,...
    -17.67,-7.3037];

D_2=[0.0000064576,0.000012269,1.08318e-17,8.50059e-18,6.375e-18,...
    9.84391e-18,1.1284e-17,1.27005e-17,1.17156e-17,9.36662e-18,...
```

```
    1.7106e-17,1.24905e-17,7.50905e-18,0.0000072244,0.01885,2.35591e-17,
    9.08906e-9,2.23859e-17,7.33561e-9,7.79511e-9,1.6898e-17,6.91060e-6,.
    1.4542e-17,1.9443e-17,0.022725,0.000013413,6.2148e-6,1.08854e-5,...
    6.95207e-9,8.41950e-9,5.538e-6,2.1702e-17,1.1492e-17,8.8865e-18,...
    6.85926e-18,1.24493e-14,0.011932,6.9844e-6,2.3248e-19,3.0582e-18,...
    8.2034e-18,0.016043,1.1406e-17,1.5835e-17,5.9208e-6,2.81115e-16,...
    1.25689e-16,1.866e-18,9.7554e-18,3.2645e-18,0.024508,9.1978e-18,...
    5.9506e-18,0.00063693,1.3402e-17,5.5501e-6,5.4574e-17,1.0073e-5,...
    2.0909e-17,2.909e-17,0.000014913,2.8856e-6,5.986e-6,8.2534e-18,...
    4.78893e-18,4.16911e-18,1.7914e-17,1.15929e-18,9.1346e-8,...
    6.3208e-6,2.37819e-6,5.64949e-18,9e-6,5.9615e-17,3.53663e-18,...
    8.792e-6,5.986e-6,4.5901e-6,3.5712e-19,5.4537e-18,2.3806e-18,...
    0.018848,3.7892e-6,1.3073e-18,2.20931e-17,0.022725,1.6898e-17,...
    4.3032e-18,3.1019e-5,7.4664e-6,2.94986e-17,1.8629e-17,1.4903e-17,...
    2.93909e-18,2.6331e-18,3.40246e-18,2.108e-17,0,...
    1.00662e-18,0,4.5e-17,8.3307e-6,7.8468e-6,0,5.66719e-19,2.02004e-18,
    7.2769e-6,0,0,2.0129e-17,1.29204e-18,0,0,8.113e-6,...
    8.1366e-6,1.9e-18,3.0231e-18,5.5643e-6,9.4509e-6,1.047e-5,...
    0,1.047e-5,1.4943e-17,0.014711,0.00002476,8.6674e-6,...
    3.6082e-18,6.3588e-18,7.1266e-6,3.9369e-18,8.0906e-6,1.6133e-5,...
    8.8382e-6,3.5456e-18,2.3171e-18,7.2099e-6,2.6734e-18,6.8172e-6,...
    1.2381e-5,2.452e-5,6.8912e-18,0.044127,4.1617e-18,7.4008e-6,...
    7.8544e-6,1.135e-5,5.9272e-6,7.1802e-6,3.0543e-18,5.6136e-6,...
    9.6171e-6,0,1.0346e-5,2.0597e-17,9.602e-6,4.8584e-6,...
    7.7485e-6,6.5877e-6,1.6324e-5,8.4197e-6,8.1871e-6,0.025182,...
    0.028405,5.9594e-6,8.6988e-18,6.8698e-18,6.2499e-18,1.019e-5,...
    1.1843e-18,5.624e-6,9.9989e-17,6.077e-6,5.2528e-6,6.7821e-18,...
    6.4319e-18,1.18202e-18,1.3703e-5,1.6242e-17,3.05212e-18,4.4315e-6,..
    5.3017e-6,0.024578,1.2363e-17,6.4481e-18,4.1653e-6];

E_2=[2.0,2.0,6.0,6.0,6.0,6.0,6.0,6.0,6.0,6.0,6.0,6.0,6.0,2.0,1.0,6.0,...
    3.0,6.0,3.0,3.0,6.0,2.0,6.0,6.0,1.0,2.0,2.0,2.0,3.0,3.0,2.0,6.0,...
    6.0,6.0,6.0,5.0,1.0,2.0,6.0,6.0,6.0,1.0,6.0,6.0,2.0,6.0,2.0,6.0,...
    6.0,6.0,1.0,6.0,6.0,1.0,6.0,2.0,6.0,2.0,6.0,6.0,2.0,2.0,2.0,6.0,...
    6.0,6.0,6.0,6.0,2.0,2.0,2.0,6.0,2.0,6.0,6.0,2.0,2.0,2.0,6.0,6.0,...
    6.0,1.0,2.0,6.0,6.0,1.0,6.0,6.0,2.0,2.0,6.0,6.0,6.0,6.0,6.0,6.0,...
    6.0,0.0,6.0,0.0,6.0,2.0,2.0,0.0,6.0,6.0,2.0,0.0,0.0,6.0,6.0,0.0,...
    0.0,2.0,2.0,6.0,6.0,2.0,2.0,2.0,2.0,2.0,6.0,1.0,2.0,2.0,6.0,6.0,...
    2.0,6.0,2.0,2.0,2.0,6.0,6.0,2.0,6.0,2.0,2.0,2.0,6.0,1.0,6.0,2.0,...
    2.0,2.0,2.0,2.0,6.0,2.0,2.0,0.0,2.0,2.0,2.0,2.0,2.0,2.0,2.0,2.0,...
    2.0,1.0,1.0,2.0,6.0,6.0,6.0,2.0,6.0,2.0,6.0,2.0,2.0,6.0,6.0,6.0,...
    2.0,6.0,6.0,2.0,2.0,1.0,6.0,6.0,2.0];

Vw_2=[46.76,40.82,52.4,113.8,105.69,134.2,83.09,72.86,64.77,93.32,85.23,
    62.63,42.17,88.69,88.6999,54.58,49.27,42.53,79.96,69.73,52.39,88.71,
    78.48,68.25,47.79,44.29,56.67,96.22,90.19,59.5,44.2,68.25,98.94,...
    33.3,54.0,39.4,60.98,48.4,65.58,68.01,47.40,28.8,49.53,54.9,90.2,...
    19.7,22.5,26.32,61.4,65.08,51.5,55.88,60.7,71.9399,46.24,50.04,...
    31.04,38.14,71.96,71.96,27.34,31.94,69.74,73.23,134.6,155.1,52.77,..
```

```
    196,83.45,38.71,22.74,114.2,63.0,61.73,175.5,34.44,69.74,80.69,...
    51.36,110.66,17.89,18.72,73.23,65.9199,49.52,47.79,52.39,65.03,...
    17.05,21.71,28.0,61.73,63.00,124.38,75.0,144.84,42.54,0.00,185.8,...
    0.000,28.48,59.49,32.51,0.000,206.2,103.9,202.7,0.000,0.000,...
    52.77,165.3,0.000,0.000,24.21,90.28,39.04,45.87,70.66,47.80,...
    73.23,0.000,73.23,59.17,63.1999,144.84,236.91,103.92,83.46,...
    109.2,231.9,129.6,334.2,211.5,221.7,283.09,78.49,272.9,170.6,68.26,.
    375.2,62.64,15.98,303.55,201.2,98.95,293.3,191,88.72,262.6,160.3,...
    58.03,0.000,63.0,48.94,52.97,73.23,252.4,150.1,313.8,242.2,119.4,...
    65.03,13.0,70.66,65.03,100.43,53.8,37.57,43.42,79.97,34.08,70.66,...
    45.5,41.79,54.34,82.8,52.38,59.15,109.02,50.58,59.51,43.5,76.03,...
    84.86,12.37]; % From DIADEM Professional

% Pure compounds' data from correlations
b_2=zeros(NC_t,1);
a0_2=zeros(NC_t,1);
Gamma_2=zeros(NC_t,1);
for i=1:NC_t
    if Vw_2(i)>0 % Some of the compounds could not be found.
    b_2(i)=(1.32e-6*Vw_2(i)^2+1.42e-3*Vw_2(i)+3.64e-3)*1000;
    a0_2(i)=1.25e-3*Vw_2(i)^2+0.34*Vw_2(i)-2.84;
    Gamma_2(i)=a0_2(i)/(8.31446261815324*b_2(i))*100000;
    end
end

% Checking if the data are OK
    if length(Tc)==length(b) && length(b)==length(Gamma) &&...
       length(Gamma)==length(c1) && length(c1)==length(epsilon) &&...
       length(epsilon)==length(beta) && length(beta)==length(scheme) &&.
       length(scheme)==length(Vw_2) && length(Vw_2)==length(Pc) &&...
       length(Pc)==length(MW)&& length(MW)==length(Gamma_2) &&...
       length(Gamma_2)==length(b_2) && length(b_2)==length(A_2)&&...
       length(A_2)==length(B_2) && length(B_2)==length(C_2) &&...
       length(C_2)==length(D_2) && length(D_2)==length(E_2) &&...
       length(E_2)==length(A_1) && length(A_1)==length(B_1) &&...
       length(B_1)==length(C_1) && length(C_1)==length(D_1) &&...
       length(D_1)==length(omega) && length(omega)==length(a0)&&...
       length(a0)==length(a0_2)
    else
       disp('WRONG DATA DIMENSIONS')
       disp(length(MW))
       disp(length(b))
       disp(length(Gamma))
       disp(length(c1))
       disp(length(epsilon))
       disp(length(beta))
       disp(length(scheme))
       disp(length(Pc))
       disp(length(Tc))
```

```
       disp(' ')
       disp(length(b_2))
       disp(length(Gamma_2))
       disp(' ')
       disp(length(A_1))
       disp(length(B_1))
       disp(length(C_1))
       disp(length(D_1))
       disp(length(A_2))
       disp(length(B_2))
       disp(length(C_2))
       disp(length(D_2))
       disp(length(E_2))
       return
    end

    % Removing the two worst points
    A_1(176)=0;
    A_1(79)=0;
    C_1(176)=0;
    C_1(79)=0;

% Using DIPPR correlations ---------------------------------------------
     Density_3=zeros(NC_t,m); % Vector saving all Liquid Densities.
     Pressure_3=zeros(NC_t,m); % Vector saving all Vapour Pressures.
     T=zeros(NC_t,m); % Vector saving all temperatures

   for i=1:NC_t
          k=round(0.45*Tc(i)/Step,0);
          if k <= 0.45*Tc(i)/Step
                for j=1:1:k+1
                         T(i,j)=0.5*Tc(i)+Step*(j-1);
                if T(i,j)<=C_1(i)&& C_1(i)>0  && i~=185
                        Density_3(i,j)=(A_1(i)/(B_1(i)^(1+(1-T(i,j)/...
                        C_1(i))^D_1(i))))*MW(i);% / kg/m3
                        Pressure_3(i,j)=exp(A_2(i)+B_2(i)/T(i,j)+C_2(i)*
                        log(T(i,j))+D_2(i)*T(i,j)^E_2(i)); % / Pa
                end

                    if i==185  && T(i,j)<=C_1(i)
                        Density_3(185,j)=(17.863+58.606*(1-T(i,j)/...
                            Tc(i))^0.35-95.396*(1-T(i,j)/Tc(i))^(2/3)+..
                            213.89*(1-T(i,j)/Tc(i))-141.26*(1-T(i,j)/...
                            Tc(i))^(4/3))*MW(185); % / kg/m3
                    Pressure_3(i,j)=exp(A_2(i)+B_2(i)/T(i,j)+C_2(i)*...
                        log(T(i,j))+D_2(i)*T(i,j)^E_2(i)); % / Pa
                    end
                end
          end
```

```
         if k > 0.45*Tc(i)/Step
                for j=1:1:k
                         T(i,j)=0.5*Tc(i)+Step*(j-1);
                if T(i,j)<=C_1(i) && C_1(i)> 0 && i~=185
                        Density_3(i,j)=(A_1(i)/(B_1(i)^(1+(1-T(i,j)/...
                        C_1(i))^D_1(i))))*MW(i);% / kg/m3
                        Pressure_3(i,j)=exp(A_2(i)+B_2(i)/T(i,j)+C_2(i)*
                        log(T(i,j))+D_2(i)*T(i,j)^E_2(i)); % / Pa
                end
                    if i==185 && T(i,j)<=C_1(i)
                        Density_3(185,j)=(17.863+58.606*(1-T(i,j)/...
                            Tc(i))^0.35-95.396*(1-T(i,j)/Tc(i))^(2/3)+..
                            213.89*(1-T(i,j)/Tc(i))-141.26*(1-T(i,j)/...
                            Tc(i))^(4/3))*MW(185); % / kg/m3
                    Pressure_3(i,j)=exp(A_2(i)+B_2(i)/T(i,j)+C_2(i)*...
                        log(T(i,j))+D_2(i)*T(i,j)^E_2(i)); % / Pa
                    end
                end
         end
  FINISHUP_THERMO();
  end

% Pure CPA EoS ---------------------------------------------------------
     Pressure_1=zeros(NC_t,m); % Vector saving all Vapour Pressures.
     ERROR_1=zeros(NC_t,m); % Vector saving all Error Codes.
     ERROR_1=ERROR_1+1;
     Density_1=zeros(NC_t,m); % Vector saving all Liquid Densities.
     T=zeros(NC_t,m); % Vector saving all temperatures

        for i=1:NC_t
          CHOOSEAMODEL(1); % 1-CPA
          NC=1;
          NOPURECOMP(NC);
          N=1; % mol
          m=410; % Number of columns.
          Step=1; % Step in temperature calculations / K
          % Association parameters
          if scheme(i)==11
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1, 011, beta(i), epsilon(i));
            elseif scheme(i)==22
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1, 022,   beta(i), epsilon(i));
            elseif scheme(i)==100
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1, 100, beta(i), epsilon(i));
            elseif scheme(i)==12
            ASSOCPARAMS(1, 012, beta(i), epsilon(i));
```

```
  elseif scheme(i)==21
  ASSOCPARAMS(1, 021, beta(i), epsilon(i));
  elseif scheme(i)==111
  ASSOCPARAMS(1, 111, beta(i), epsilon(i));
  elseif scheme(i)==110
  ASSOCPARAMS(1, 110, beta(i), epsilon(i));
end
% Critical properties
CRITPROPS(1, Tc(i), Pc2(i),omega(i));

% CPA parameters
       % idx b0 Gamma c1
CPAPARAMS(1,b(i),Gamma(i),c1(i));

% Finishing setup
SETUP_THERMO()

k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
      for j=1:1:k+1
               T(i,j)=0.5*Tc(i)+Step*(j-1);
      if T(i,j)<=C_1(i) && C_1(i)>0
          [P,~,IERR]=PBUBBLE(T(i,j),N);
              if (IERR~=0 && j>1)  % Initial guess
              [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_1(i,j-1));
              end
              ERROR_1(i,j)=IERR;
              if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
                      Pressure_3(i,j)>0
              Pressure_1(i,j)=P; % Vapour pressure / Pa
              [ZFact,~]=FUGACITY(T(i,j),P,N,1);
              Density_1(i,j)=Pressure_1(i,j)...
                  /(ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
              % Density / kg/m3
              end
      end
      end
end
if k > 0.45*Tc(i)/Step
      for j=1:1:k
          T(i,j)=0.5*Tc(i)+Step*(j-1);
      if T(i,j)<=C_1(i) && C_1(i)>0
          [P,~,IERR]=PBUBBLE(T(i,j),N);
          if IERR~=0 && j>1  % Initial guess
              [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_1(i,j-1));
          end
              ERROR_1(i,j)=IERR;
          if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
                      Pressure_3(i,j)>0
```

```
                        Pressure_1(i,j)=P; % Vapour pressure / Pa
                        [ZFact,~]=FUGACITY(T(i,j),P,N,1);
                        Density_1(i,j)=Pressure_1(i,j)/...
                            (ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
                        % Density / kg/m3
                    end
                end
                end
          end
 FINISHUP_THERMO();
        end

% Correlated a0 and b --------------------------------------------------
     Pressure_2=zeros(NC_t,m); % Vector saving all Vapour Pressures.
     ERROR_2=zeros(NC_t,m); % Vector saving all Error Codes.
     ERROR_2=ERROR_2+1;
     Density_2=zeros(NC_t,m); % Vector saving all Liquid densities.
     T=zeros(NC_t,m); % Vector saving all temperatures

  for i=1:NC_t
          CHOOSEAMODEL(1); % 1-CPA
          NC=1;
          NOPURECOMP(NC);
          N=1; % mol
          Step=1; % Step in temperature calculations / K
          % Association parameters
          if scheme(i)==11
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1, 011, beta(i), epsilon(i));
            elseif scheme(i)==22
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1, 022, beta(i), epsilon(i));
            elseif scheme(i)==100
                     % idx scheme ass.volume ass.energy
            ASSOCPARAMS(1,100, beta(i), epsilon(i));
            elseif scheme(i)==12
            ASSOCPARAMS(1, 012, beta(i), epsilon(i));
            elseif scheme(i)==21
            ASSOCPARAMS(1, 021, beta(i), epsilon(i));
            elseif scheme(i)==111
            ASSOCPARAMS(1, 111, beta(i), epsilon(i));
            elseif scheme(i)==110
            ASSOCPARAMS(1, 110, beta(i), epsilon(i));
          end

          % Critical properties
          CRITPROPS(1, Tc(i), Pc2(i), omega(i));

          % CPA parameters
```

```
        % idx b0 Gamma c1
 CPAPARAMS(1,b_2(i),Gamma_2(i),c1(i));

 % Finishing setup
 SETUP_THERMO()

 k=round(0.45*Tc(i)/Step,0);
 if k <= 0.45*Tc(i)/Step
       for j=1:1:k+1
                T(i,j)=0.5*Tc(i)+Step*(j-1);
       if T(i,j)<=C_1(i) && C_1(i)>0
           [P,~,IERR]=PBUBBLE(T(i,j),N);
               if IERR~=0 && j>1  % Initial guess
               [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_2(i,j-1));
               end
               ERROR_2(i,j)=IERR;
               if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
                       Pressure_3(i,j)>0
               Pressure_2(i,j)=P; % Vapour pressure / Pa
               [ZFact,~]=FUGACITY(T(i,j),P,N,1);
               Density_2(i,j)=Pressure_2(i,j)/...
                   (ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
               % Density / kg/m3
               end
       end
       end
 end

if k > 0.45*Tc(i)/Step
       for j=1:1:k
                T(i,j)=0.5*Tc(i)+Step*(j-1);
       if T(i,j)<=C_1(i) && C_1(i)>0
           [P,~,IERR]=PBUBBLE(T(i,j),N);
               if IERR~=0 && j>1  % Initial guess
               [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_2(i,j-1));
               end
               ERROR_2(i,j)=IERR;
               if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
                       Pressure_3(i,j)>0
               Pressure_2(i,j)=P; % Vapour pressure / Pa
               [ZFact,~]=FUGACITY(T(i,j),P,N,1);
               Density_2(i,j)=Pressure_2(i,j)/...
                   (ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
               % Density / kg/m3
               end
       end
       end
end
 FINISHUP_THERMO();
```

```
  end

% Correlated a0 and b and fitted c1 ------------------------------------
    function [fval]=fit(x0,A,scheme,beta,epsilon,Tc,Pc2,omega,b_2,...
            Gamma_2,C_1,Density_3,Pressure_3,MW)

          ii=A;
          CHOOSEAMODEL(1); % 1-CPA
          NC2=1;
          NOPURECOMP(NC2);
          N2=1; % mol
          m2=410; % Number of columns.
          NC_t2=185;
          Step2=1; % Step in temperature calculations / K
          Pressure_41=zeros(NC_t2,m2); % Vector saving all Vapour Pressu
          ERROR_41=zeros(NC_t2,m2); % Vector saving all Error Codes.
          ERROR_41=ERROR_41+1;
          % Liquid density
          Density_41=zeros(NC_t2,m2); % Vector saving all Densities.
          % Vector saving all temperatures
          TT=zeros(NC_t2,m2);
          % Vector saving all quadratic errors
          quaderror=zeros(NC_t2,m2);

          if scheme(ii)==11
            ASSOCPARAMS(1, 011, beta(ii), epsilon(ii));
            elseif scheme(ii)==22
            ASSOCPARAMS(1, 022,   beta(ii), epsilon(ii));
            elseif scheme(ii)==100
            ASSOCPARAMS(1, 100, beta(ii), epsilon(ii));
            elseif scheme(ii)==12
            ASSOCPARAMS(1, 012, beta(ii), epsilon(ii));
            elseif scheme(ii)==21
            ASSOCPARAMS(1, 021, beta(ii), epsilon(ii));
            elseif scheme(ii)==111
            ASSOCPARAMS(1, 111, beta(ii), epsilon(ii));
            elseif scheme(ii)==110
            ASSOCPARAMS(1, 110, beta(ii), epsilon(ii));
          end

          % Critical properties
          CRITPROPS(1, Tc(ii), Pc2(ii),omega(ii));

          % CPA parameters
          CPAPARAMS(1,b_2(ii),Gamma_2(ii),x0(1));

          % Finishing setup
          SETUP_THERMO()
```

```
kk=round(0.45*Tc(ii)/Step2,0);
if kk <= 0.45*Tc(ii)/Step2
      for jj=1:1:kk+1
               TT(ii,jj)=0.5*Tc(ii)+Step2*(jj-1);
      if TT(ii,jj)<=C_1(ii)  && C_1(ii)>0
          [P2,~,IERR2]=PBUBBLE(TT(ii,jj),N2);
              if IERR2~=0  && jj>1  % Initial guess
              [P2,~,IERR2]=PBUBBLE(TT(ii,jj),N2,...
                  Pressure_41(ii,jj-1));
              end
              ERROR_41(ii,jj)=IERR2;
              if ERROR_41(ii,jj)==0  && Density_3(ii,jj)>0 ...
                      && Pressure_3(ii,jj)>0
              Pressure_41(ii,jj)=P2;
              [ZFact2,~]=FUGACITY(TT(ii,jj),P2,N2,1);
              Density_41(ii,jj)=Pressure_41(ii,jj)/(ZFact2*...
                  8.31446261815324*TT(ii,jj)*1000)*MW(ii);
              quaderror(ii,jj)=((Density_41(ii,jj)-...
                  Density_3(ii,jj))/Density_3(ii,jj))^2+...
                  ((Pressure_41(ii,jj)-Pressure_3(ii,jj))/...
                  Pressure_3(ii,jj))^2;
              end
      end
      end
      B=sum(quaderror,2);
      QE_mean(ii)=B(ii)/(kk+1);
end
if kk > 0.45*Tc(ii)/Step2
      for jj=1:1:kk
          TT(ii,jj)=0.5*Tc(ii)+Step2*(jj-1);
        if TT(ii,jj)<=C_1(ii)&& C_1(ii)>0
          [P2,~,IERR2]=PBUBBLE(TT(ii,jj),N2);
              if IERR2~=0  && jj>1   % Initial guess
              [P2,~,IERR2]=PBUBBLE(TT(ii,jj),N2,...
                  Pressure_41(ii,jj-1));
              end
              ERROR_41(ii,jj)=IERR2;
              if ERROR_41(ii,jj)==0  && Density_3(ii,jj)>0  &&..
                      Pressure_3(ii,jj)>0
              Pressure_41(ii,jj)=P2;
              [ZFact2,~]=FUGACITY(TT(ii,jj),P2,N2,1);
              Density_41(ii,jj)=Pressure_41(ii,jj)/...
                 (ZFact2*8.31446261815324*TT(ii,jj)*1000)*MW(i
              quaderror(ii,jj)=((Density_41(ii,jj)-...
                  Density_3(ii,jj))/Density_3(ii,jj))^2+...
                  ((Pressure_41(ii,jj)-Pressure_3(ii,jj))/...
                  Pressure_3(ii,jj))^2;
              end
        end
```

```
            end
            B=sum(quaderror,2);
            QE_mean(ii)=B(ii)/kk;
      end
      fval=QE_mean(ii);
      FINISHUP_THERMO();
end
NC_t=185;
for i=1:NC_t
 A=i;
 y = @(x0)fit(x0,A,scheme,beta,epsilon,Tc,Pc2,omega,b_2,...
        Gamma_2,C_1,Density_3,Pressure_3,MW);
 x0(1)=c1(i);
 lb = 0;
 ub = 2;
 options = optimoptions('fmincon','Display', 'off');
 [x, fval] = fmincon(y,x0,[],[],[],[],lb,ub,[],options);
 c1_f(i)=x(1);
 QE(i)=fval;
end

 NC_t=185;
 m=410; % Number of columns.
 Step=1; % Step in temperature calculations / K
 Pressure_4=zeros(NC_t,m); % Vector saving all Vapour Pressures.
 ERROR_4=zeros(NC_t,m); % Vector saving all Error Codes.
 ERROR_4=ERROR_4+1;
 Density_4=zeros(NC_t,m); % Vector saving all Densities.
 T=zeros(NC_t,m); % Vector saving all temperatures

    for i=1:NC_t
      CHOOSEAMODEL(1); % 1-CPA
      NC=1;
      NOPURECOMP(NC);
      N=1; % mol
      Step=1; % Step in temperature calculations / K
      % Association parameters
      if scheme(i)==11
                 % idx scheme ass.volume ass.energy
        ASSOCPARAMS(1, 011, beta(i), epsilon(i));
        elseif scheme(i)==22
                 % idx scheme ass.volume ass.energy
        ASSOCPARAMS(1, 022,   beta(i), epsilon(i));
        elseif scheme(i)==100
                 % idx scheme ass.volume ass.energy
        ASSOCPARAMS(1, 100, beta(i), epsilon(i));
        elseif scheme(i)==12
        ASSOCPARAMS(1, 012, beta(i), epsilon(i));
        elseif scheme(i)==21
```

```
  ASSOCPARAMS(1, 021, beta(i), epsilon(i));
  elseif scheme(i)==111
  ASSOCPARAMS(1, 111, beta(i), epsilon(i));
  elseif scheme(i)==110
  ASSOCPARAMS(1, 110, beta(i), epsilon(i));
end
% Critical properties
CRITPROPS(1, Tc(i), Pc2(i),omega(i));

% CPA parameters
       % idx b0 Gamma c1
CPAPARAMS(1,b_2(i),Gamma_2(i),c1_f(i));

% Finishing setup
SETUP_THERMO()
k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
      for j=1:1:k+1
               T(i,j)=0.5*Tc(i)+Step*(j-1);
          if  C_1(i)>0 && T(i,j)<=C_1(i)
          [P,~,IERR]=PBUBBLE(T(i,j),N);
          if IERR~=0 && j>1  % Initial guess
              [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_4(i,j-1));
          end
          ERROR_4(i,j)=IERR;
              if ERROR_4(i,j)==0
              Pressure_4(i,j)=P; % Vapour pressure / Pa
              [ZFact,~]=FUGACITY(T(i,j),P,N,1);
              Density_4(i,j)=Pressure_4(i,j)...
                  /(ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
              % Density / kg/m3
              end
          end
      end
end
if k > 0.45*Tc(i)/Step
      for j=1:1:k
          T(i,j)=0.5*Tc(i)+Step*(j-1);
          if  C_1(i)>0 && T(i,j)<=C_1(i)
          [P,~,IERR]=PBUBBLE(T(i,j),N);
          if IERR~=0 && j>1  % Initial guess
              [P,~,IERR]=PBUBBLE(T(i,j),N,Pressure_4(i,j-1));
          end
          ERROR_4(i,j)=IERR;
              if ERROR_4(i,j)==0
              Pressure_4(i,j)=P; % Vapour pressure / Pa
              [ZFact,~]=FUGACITY(T(i,j),P,N,1);
              Density_4(i,j)=Pressure_4(i,j)/...
                  (ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
```

```
                        % Density / kg/m3
                        end
                    end
                end
          end
          FINISHUP_THERMO();
        end

% Correlated b and fitted Gamma and c1 ---------------------------------
    function [fval]=fit2(x0_2,A,scheme,beta,epsilon,Tc,Pc2,omega,b_2,...
            C_1,Density_3,Pressure_3,MW)

          ii=A;
          CHOOSEAMODEL(1); % 1-CPA
          NC3=1;
          NOPURECOMP(NC3);
          N3=1; % mol
          m3=410; % Number of columns.
          NC_t3=185;
          Step3=1; % Step in temperature calculations / K
          Pressure_51=zeros(NC_t3,m3); % Vector saving all Vapour Pressu
          ERROR_51=zeros(NC_t3,m3); % Vector saving all Error Codes.
          ERROR_51=ERROR_51+1;
          % Liquid density
          Density_51=zeros(NC_t3,m3); % Vector saving all Densities.
          % Vector saving all temperatures
          TT=zeros(NC_t3,m3);
          % Vector saving all quadratic errors
          quaderror=zeros(NC_t3,m3);

          if scheme(ii)==11
            ASSOCPARAMS(1, 011, beta(ii), epsilon(ii));
            elseif scheme(ii)==22
            ASSOCPARAMS(1, 022,   beta(ii), epsilon(ii));
            elseif scheme(ii)==100
            ASSOCPARAMS(1, 100, beta(ii), epsilon(ii));
            elseif scheme(ii)==12
            ASSOCPARAMS(1, 012, beta(ii), epsilon(ii));
            elseif scheme(ii)==21
            ASSOCPARAMS(1, 021, beta(ii), epsilon(ii));
            elseif scheme(ii)==111
            ASSOCPARAMS(1, 111, beta(ii), epsilon(ii));
            elseif scheme(ii)==110
            ASSOCPARAMS(1, 110, beta(ii), epsilon(ii));
          end

          % Critical properties
          CRITPROPS(1, Tc(ii), Pc2(ii),omega(ii));
```

```
% CPA parameters
CPAPARAMS(1,b_2(ii),x0_2(1),x0_2(2));

% Finishing setup
SETUP_THERMO()

kk=round(0.45*Tc(ii)/Step3,0);
if kk <= 0.45*Tc(ii)/Step3
      for jj=1:1:kk+1
               TT(ii,jj)=0.5*Tc(ii)+Step3*(jj-1);
          if  C_1(ii)>0 && TT(ii,jj)<=C_1(ii)
          [P3,~,IERR3]=PBUBBLE(TT(ii,jj),N3);
              if IERR3~=0 && jj>1  % Initial guess
              [P3,~,IERR3]=PBUBBLE(TT(ii,jj),N3,...
                  Pressure_51(ii,jj-1));
              end
              ERROR_51(ii,jj)=IERR3;
              if ERROR_51(ii,jj)==0 && Density_3(ii,jj)>0 ...
                      && Pressure_3(ii,jj)>0
              Pressure_51(ii,jj)=P3;
              [ZFact3,~]=FUGACITY(TT(ii,jj),P3,N3,1);
              Density_51(ii,jj)=Pressure_51(ii,jj)/(ZFact3*...
                  8.31446261815324*TT(ii,jj)*1000)*MW(ii);
              quaderror(ii,jj)=((Density_51(ii,jj)-...
                  Density_3(ii,jj))/ Density_3(ii,jj))^2+...
                  ((Pressure_51(ii,jj)-Pressure_3(ii,jj))/...
                  Pressure_3(ii,jj))^2;
              end
          end
      end
      B=sum(quaderror,2);
      QE_mean(ii)=B(ii)/(kk+1);
end
if kk > 0.45*Tc(ii)/Step3
      for jj=1:1:kk
          TT(ii,jj)=0.5*Tc(ii)+Step3*(jj-1);
          if  C_1(ii)>0 && TT(ii,jj)<=C_1(ii)
          [P3,~,IERR3]=PBUBBLE(TT(ii,jj),N3);
              if IERR3~=0 && jj>1  % Initial guess
              [P3,~,IERR3]=PBUBBLE(TT(ii,jj),N3,...
                  Pressure_51(ii,jj-1));
              end
              ERROR_51(ii,jj)=IERR3;
              if ERROR_51(ii,jj)==0 && Density_3(ii,jj)>0 &&..
                      Pressure_3(ii,jj)>0
              Pressure_51(ii,jj)=P3; % Vapour pressure / Pa
              [ZFact3,~]=FUGACITY(TT(ii,jj),P3,N3,1);
              Density_51(ii,jj)=Pressure_51(ii,jj)/...
                 (ZFact3*8.31446261815324*TT(ii,jj)*1000)*MW(i
```

```
                    % Density / kg/m3
                    quaderror(ii,jj)=((Density_51(ii,jj)-...
                        Density_3(ii,jj))/Density_3(ii,jj))^2+...
                        ((Pressure_51(ii,jj)-Pressure_3(ii,jj))/...
                        Pressure_3(ii,jj))^2;
                    end
                end
            end
            B=sum(quaderror,2);
            QE_mean(ii)=B(ii)/kk;
      end
      fval=QE_mean(ii);
      FINISHUP_THERMO();
end
NC_t=185;
for i=1:NC_t
 A=i;
 y = @(x0_2)fit2(x0_2,A,scheme,beta,epsilon,Tc,Pc2,omega,b_2,...
        C_1,Density_3,Pressure_3,MW);
 x0_2(1)=Gamma(i);
 x0_2(2)=c1(i);
 lb = [0;0];
 ub = [5000;2];
 options = optimoptions('fmincon','Display', 'off');
 [x_2, fval] = fmincon(y,x0_2,[],[],[],[],lb,ub,[],options);
 Gamma_f2(i)=x_2(1);
 c1_f2(i)=x_2(2);
 QE(i)=fval;
end

 NC_t=185;
 m=410; % Number of columns.
 Pressure_5=zeros(NC_t,m); % Vector saving all Vapour Pressures.
 ERROR_5=zeros(NC_t,m); % Vector saving all Error Codes.
 ERROR_5=ERROR_5+1;
 % Liquid density
 Density_5=zeros(NC_t,m); % Vector saving all Densities.
 % Vector saving all temperatures
 T=zeros(NC_t,m);

    for i=1:NC_t
      CHOOSEAMODEL(1); % 1-CPA
      NC=1;
      NOPURECOMP(NC);
      N=1; % mol
      Step=1; % Step in temperature calculations / K
      % Association parameters
      if scheme(i)==11
                 % idx scheme ass.volume ass.energy
```

```
  ASSOCPARAMS(1, 011, beta(i), epsilon(i));
  elseif scheme(i)==22
           % idx scheme ass.volume ass.energy
  ASSOCPARAMS(1, 022,   beta(i), epsilon(i));
  elseif scheme(i)==100
           % idx scheme ass.volume ass.energy
  ASSOCPARAMS(1, 100, beta(i), epsilon(i));
  elseif scheme(i)==12
  ASSOCPARAMS(1, 012, beta(i), epsilon(i));
  elseif scheme(i)==21
  ASSOCPARAMS(1, 021, beta(i), epsilon(i));
  elseif scheme(i)==111
  ASSOCPARAMS(1, 111, beta(i), epsilon(i));
  elseif scheme(i)==110
  ASSOCPARAMS(1, 110, beta(i), epsilon(i));
end
% Critical properties
CRITPROPS(1, Tc(i), Pc2(i),omega(i));

% CPA parameters
       % idx b0 Gamma c1
CPAPARAMS(1,b_2(i),Gamma_f2(i),c1_f2(i));

% Finishing setup
SETUP_THERMO()
k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
      for j=1:1:k+1
               T(i,j)=0.5*Tc(i)+Step*(j-1);
          if  C_1(i)>0 && T(i,j)<=C_1(i)
          [P,~,IERR]=PBUBBLE(T(i,j),N);
          if IERR~=0 && j>1  % Initial guess
              [P,~,IERR]=PBUBBLE(T(i,j),N,...
                  Pressure_5(i,j-1));
          end
          ERROR_5(i,j)=IERR;
              if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
                      Pressure_3(i,j)>0
              Pressure_5(i,j)=P; % Vapour pressure / Pa
              [ZFact,~]=FUGACITY(T(i,j),P,N,1);
              Density_5(i,j)=Pressure_5(i,j)...
                  /(ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
              % Density / kg/m3
              end
          end
      end
end
if k > 0.45*Tc(i)/Step
      for j=1:1:k
```

```
                    T(i,j)=0.5*Tc(i)+Step*(j-1);
                    if  C_1(i)>0 && T(i,j)<=C_1(i)
                    [P,~,IERR]=PBUBBLE(T(i,j),N);
                    if IERR~=0 && j>1  % Initial guess
                        [P,~,IERR]=PBUBBLE(T(i,j),N,...
                            Pressure_5(i,j-1));
                    end
                    ERROR_5(i,j)=IERR;
                        if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
                                Pressure_3(i,j)>0
                        Pressure_5(i,j)=P; % Vapour pressure / Pa
                        [ZFact,~]=FUGACITY(T(i,j),P,N,1);
                        Density_5(i,j)=Pressure_5(i,j)/...
                            (ZFact*8.31446261815324*T(i,j)*1000)*MW(i);
                        % Density / kg/m3
                        end
                    end
                end
          end
          FINISHUP_THERMO();
        end
% Analysing results ---------------------------------------------------.
n_1=0;
n_2=0;
n_4=0;
n_5=0;
AD_1d=zeros(NC_t,m);
AD_2d=zeros(NC_t,m);
AD_4d=zeros(NC_t,m);
AD_5d=zeros(NC_t,m);
AD_1p=zeros(NC_t,m);
AD_2p=zeros(NC_t,m);
AD_4p=zeros(NC_t,m);
AD_5p=zeros(NC_t,m);
nn_1=zeros(NC_t,m);
nn_2=zeros(NC_t,m);
nn_4=zeros(NC_t,m);
nn_5=zeros(NC_t,m);

for i=1:NC_t
k=round(0.45*Tc(i)/Step,0);
    if k <= 0.45*Tc(i)/Step
          for j=1:1:k+1
                if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
                        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                        && i~=79
                    n_1=n_1+1;
                    nn_1(i,j)=1;
                end
```

```
if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    n_2=n_2+1;
    nn_2(i,j)=1;
end
if ERROR_4(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    n_4=n_4+1;
    nn_4(i,j)=1;
end
if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    n_5=n_5+1;
    nn_5(i,j)=1;
end
if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    AD_1d(i,j)=abs(Density_1(i,j)-Density_3(i,j))/...
        Density_3(i,j)*100;
    AD_1p(i,j)=abs((Pressure_1(i,j)-Pressure_3(i,j)))...
        /Pressure_3(i,j)*100;
end
if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    AD_2d(i,j)=abs((Density_2(i,j)-Density_3(i,j)))/...
        Density_3(i,j)*100;
    AD_2p(i,j)=abs((Pressure_2(i,j)-Pressure_3(i,j)))...
        /Pressure_3(i,j)*100;
end
if ERROR_4(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    AD_4d(i,j)=abs((Density_4(i,j)-Density_3(i,j)))/...
        Density_3(i,j)*100;
    AD_4p(i,j)=abs((Pressure_4(i,j)-Pressure_3(i,j)))...
        /Pressure_3(i,j)*100;
end
if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
        && i~=79
    AD_5d(i,j)=abs((Density_5(i,j)-Density_3(i,j)))/...
        Density_3(i,j)*100;
    AD_5p(i,j)=abs((Pressure_5(i,j)-Pressure_3(i,j)))...
        /Pressure_3(i,j)*100;
```

```
            end
      end
end

if k > 0.45*Tc(i)/Step
      for j=1:1:k
           if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                n_1=n_1+1;
                nn_1(i,j)=1;
            end
            if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                n_2=n_2+1;
                nn_2(i,j)=1;
            end
            if ERROR_4(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                n_4=n_4+1;
                nn_4(i,j)=1;
            end
            if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                n_5=n_5+1;
                nn_5(i,j)=1;
            end
            if ERROR_1(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                AD_1d(i,j)=abs(Density_1(i,j)-Density_3(i,j))/...
                    Density_3(i,j)*100;
                AD_1p(i,j)=abs((Pressure_1(i,j)-Pressure_3(i,j)))...
                    /Pressure_3(i,j)*100;
            end
            if ERROR_2(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                    && i~=79
                AD_2d(i,j)=abs((Density_2(i,j)-Density_3(i,j)))/...
                    Density_3(i,j)*100;
                AD_2p(i,j)=abs((Pressure_2(i,j)-Pressure_3(i,j)))...
                    /Pressure_3(i,j)*100;
            end

            if ERROR_4(i,j)==0 && Density_3(i,j)>0 &&...
                    Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
```

```
                        && i~=79
                    AD_4d(i,j)=abs((Density_4(i,j)-Density_3(i,j)))/...
                        Density_3(i,j)*100;
                    AD_4p(i,j)=abs((Pressure_4(i,j)-Pressure_3(i,j)))...
                        /Pressure_3(i,j)*100;
                end
                if ERROR_5(i,j)==0 && Density_3(i,j)>0 &&...
                        Pressure_3(i,j)>0 && T(i,j)<=C_1(i) && i~= 176 .
                        && i~=79
                    AD_5d(i,j)=abs((Density_5(i,j)-Density_3(i,j)))/...
                        Density_3(i,j)*100;
                    AD_5p(i,j)=abs((Pressure_5(i,j)-Pressure_3(i,j)))...
                        /Pressure_3(i,j)*100;
                end
          end
    end
end

% Average Absolute Deviations / %
AAD_1d=sum(real(AD_1d),'all')/n_1;
AAD_2d=sum(AD_2d,'all')/n_2;
AAD_4d=sum(AD_4d,'all')/n_4;
AAD_5d=sum(AD_5d,'all')/n_5;
AAD_1p=sum(AD_1p,'all')/n_1;
AAD_2p=sum(AD_2p,'all')/n_2;
AAD_4p=sum(AD_4p,'all')/n_4;
AAD_5p=sum(AD_5p,'all')/n_5;

% Average Absolute Deviations per chemical compound / %
rowMean_1d = sum(real(AD_1d),2)./sum(nn_1,2);
rowMean_2d = sum(real(AD_2d),2)./sum(nn_2,2);
rowMean_4d = sum(real(AD_4d),2)./sum(nn_4,2);
rowMean_5d = sum(real(AD_5d),2)./sum(nn_5,2);
rowMean_1p = sum(real(AD_1p),2)./sum(nn_1,2);
rowMean_2p = sum(real(AD_2p),2)./sum(nn_2,2);
rowMean_4p = sum(real(AD_4p),2)./sum(nn_4,2);
rowMean_5p = sum(real(AD_5p),2)./sum(nn_5,2);

% Finding the smallest Absolute Deviations
[Min_1d,I_1d] = min(rowMean_1d);
[Min_2d,I_2d] = min(rowMean_2d);
[Min_4d,I_4d] = min(rowMean_4d);
[Min_5d,I_5d] = min(rowMean_5d);
[Min_1p,I_1p] = min(rowMean_1p);
[Min_2p,I_2p] = min(rowMean_2p);
[Min_4p,I_4p] = min(rowMean_4p);
[Min_5p,I_5p] = min(rowMean_5p);

% Finding the biggest Absolute Deviations
```

```
[Max_1d,I_1dm] = max(rowMean_1d);
[Max_2d,I_2dm] = max(rowMean_2d);
[Max_4d,I_4dm] = max(rowMean_4d);
[Max_5d,I_5dm] = max(rowMean_5d);
[Max_1p,I_1pm] = max(rowMean_1p);
[Max_2p,I_2pm] = max(rowMean_2p);
[Max_4p,I_4pm] = max(rowMean_4p);
[Max_5p,I_5pm] = max(rowMean_5p);

% Behaviour in each chemical family
% -- Alcohols
v1=[3,4,6,7,8,10,12,13,16,21,28,31,62,87,90,177];
for i=v1
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B1(i,j)=AD_1d(i,j);
        D1(i,j)=AD_1p(i,j);
        F1(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C1(i,j)=AD_2d(i,j);
        E1(i,j)=AD_2p(i,j);
        G1(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H1(i,j)=AD_4d(i,j);
        I1(i,j)=AD_4p(i,j);
        J1(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R1(i,j)=AD_5d(i,j);
        S1(i,j)=AD_5p(i,j);
        T1(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B1(i,j)=AD_1d(i,j);
        D1(i,j)=AD_1p(i,j);
        F1(i,j)=nn_1(i,j);
        end
```

```
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C1(i,j)=AD_2d(i,j);
        E1(i,j)=AD_2p(i,j);
        G1(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H1(i,j)=AD_4d(i,j);
        I1(i,j)=AD_4p(i,j);
        J1(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R1(i,j)=AD_5d(i,j);
        S1(i,j)=AD_5p(i,j);
        T1(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_alcohols=sum(B1)/sum(F1);
AAD_2d_alcohols=sum(C1)/sum(G1);
AAD_4d_alcohols=sum(H1)/sum(J1);
AAD_5d_alcohols=sum(R1)/sum(T1);
AAD_1p_alcohols=sum(D1)/sum(F1);
AAD_2p_alcohols=sum(E1)/sum(G1);
AAD_4p_alcohols=sum(I1)/sum(J1);
AAD_5p_alcohols=sum(S1)/sum(T1);

% -- Alkanes
v2=[14,15,22,23,24,25,32,33,61,86,89,119,129,130,131,132,133,134,135,136
    137,138,139,140,143,144,149,150,151,152,153,154,155,165,166,167,...
    168,169,180];
for i=v2
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B2(i,j)=AD_1d(i,j);
        D2(i,j)=AD_1p(i,j);
        F2(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C2(i,j)=AD_2d(i,j);
        E2(i,j)=AD_2p(i,j);
        G2(i,j)=nn_2(i,j);
```

```
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H2(i,j)=AD_4d(i,j);
        I2(i,j)=AD_4p(i,j);
        J2(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R2(i,j)=AD_5d(i,j);
        S2(i,j)=AD_5p(i,j);
        T2(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
         if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B2(i,j)=AD_1d(i,j);
        D2(i,j)=AD_1p(i,j);
        F2(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C2(i,j)=AD_2d(i,j);
        E2(i,j)=AD_2p(i,j);
        G2(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H2(i,j)=AD_4d(i,j);
        I2(i,j)=AD_4p(i,j);
        J2(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R2(i,j)=AD_5d(i,j);
        S2(i,j)=AD_5p(i,j);
        T2(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_alkanes=sum(B2)/sum(F2);
AAD_2d_alkanes=sum(C2)/sum(G2);
AAD_4d_alkanes=sum(H2)/sum(J2);
AAD_5d_alkanes=sum(R2)/sum(T2);
AAD_1p_alkanes=sum(D2)/sum(F2);
AAD_2p_alkanes=sum(E2)/sum(G2);
```

```
AAD_4p_alkanes=sum(I2)/sum(J2);
AAD_5p_alkanes=sum(S2)/sum(T2);

% -- Amines
v3=[24,44,50,52,76,95,114,116,173,183];
for i=v3
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
       if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B3(i,j)=AD_1d(i,j);
        D3(i,j)=AD_1p(i,j);
        F3(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C3(i,j)=AD_2d(i,j);
        E3(i,j)=AD_2p(i,j);
        G3(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H3(i,j)=AD_4d(i,j);
        I3(i,j)=AD_4p(i,j);
        J3(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R3(i,j)=AD_5d(i,j);
        S3(i,j)=AD_5p(i,j);
        T3(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
       if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B3(i,j)=AD_1d(i,j);
        D3(i,j)=AD_1p(i,j);
        F3(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C3(i,j)=AD_2d(i,j);
        E3(i,j)=AD_2p(i,j);
        G3(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
```

```
                && T(i,j)<=C_1(i)
        H3(i,j)=AD_4d(i,j);
        I3(i,j)=AD_4p(i,j);
        J3(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R3(i,j)=AD_5d(i,j);
        S3(i,j)=AD_5p(i,j);
        T3(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_amines=sum(B3)/sum(F3);
AAD_2d_amines=sum(C3)/sum(G3);
AAD_4d_amines=sum(H3)/sum(J3);
AAD_5d_amines=sum(R3)/sum(T3);
AAD_1p_amines=sum(D3)/sum(F3);
AAD_2p_amines=sum(E3)/sum(G3);
AAD_4p_amines=sum(I3)/sum(J3);
AAD_5p_amines=sum(S3)/sum(T3);

% -- Aromatics
v4=[37,38,39,40,45,63,77,80,84,88,118,141,162,164,165,166,167,170,172,..
    181];
for i=v4
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B4(i,j)=AD_1d(i,j);
        D4(i,j)=AD_1p(i,j);
        F4(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C4(i,j)=AD_2d(i,j);
        E4(i,j)=AD_2p(i,j);
        G4(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H4(i,j)=AD_4d(i,j);
        I4(i,j)=AD_4p(i,j);
        J4(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
```

```
                && T(i,j)<=C_1(i)
        R4(i,j)=AD_5d(i,j);
        S4(i,j)=AD_5p(i,j);
        T4(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B4(i,j)=AD_1d(i,j);
        D4(i,j)=AD_1p(i,j);
        F4(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C4(i,j)=AD_2d(i,j);
        E4(i,j)=AD_2p(i,j);
        G4(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H4(i,j)=AD_4d(i,j);
        I4(i,j)=AD_4p(i,j);
        J4(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R4(i,j)=AD_5d(i,j);
        S4(i,j)=AD_5p(i,j);
        T4(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_aromatics=sum(B4)/sum(F4);
AAD_2d_aromatics=sum(C4)/sum(G4);
AAD_4d_aromatics=sum(H4)/sum(J4);
AAD_5d_aromatics=sum(R4)/sum(T4);
AAD_1p_aromatics=sum(D4)/sum(F4);
AAD_2p_aromatics=sum(E4)/sum(G4);
AAD_4p_aromatics=sum(I4)/sum(J4);
AAD_5p_aromatics=sum(S4)/sum(T4);

% -- Esters
v5=[55,64,65,66,67,68,69,71,72,73,83,94,96,97,98,99,100,102,103,104,105,
    106,107,108,109,110,111,112,113,120,121,122,124,125,126,127,128,152,
    153,155,93,75,156];
for i=v5
```

```
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B5(i,j)=AD_1d(i,j);
        D5(i,j)=AD_1p(i,j);
        F5(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C5(i,j)=AD_2d(i,j);
        E5(i,j)=AD_2p(i,j);
        G5(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H5(i,j)=AD_4d(i,j);
        I5(i,j)=AD_4p(i,j);
        J5(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R5(i,j)=AD_5d(i,j);
        S5(i,j)=AD_5p(i,j);
        T5(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0  ...
                && T(i,j)<=C_1(i)
        B5(i,j)=AD_1d(i,j);
        D5(i,j)=AD_1p(i,j);
        F5(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C5(i,j)=AD_2d(i,j);
        E5(i,j)=AD_2p(i,j);
        G5(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H5(i,j)=AD_4d(i,j);
        I5(i,j)=AD_4p(i,j);
        J5(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
```

```
                && T(i,j)<=C_1(i)
            R5(i,j)=AD_5d(i,j);
            S5(i,j)=AD_5p(i,j);
            T5(i,j)=nn_5(i,j);
            end
        end
end
end
AAD_1d_esters=sum(B5)/sum(F5);
AAD_2d_esters=sum(C5)/sum(G5);
AAD_4d_esters=sum(H5)/sum(J5);
AAD_5d_esters=sum(R5)/sum(T5);
AAD_1p_esters=sum(D5)/sum(F5);
AAD_2p_esters=sum(E5)/sum(G5);
AAD_4p_esters=sum(I5)/sum(J5);
AAD_5p_esters=sum(S5)/sum(T5);

% -- Polyols
v6=[1,53,117,179,184];
for i=v6
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
            B6(i,j)=AD_1d(i,j);
            D6(i,j)=AD_1p(i,j);
            F6(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
            C6(i,j)=AD_2d(i,j);
            E6(i,j)=AD_2p(i,j);
            G6(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
            H6(i,j)=AD_4d(i,j);
            I6(i,j)=AD_4p(i,j);
            J6(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
            R6(i,j)=AD_5d(i,j);
            S6(i,j)=AD_5p(i,j);
            T6(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
```

```
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B6(i,j)=AD_1d(i,j);
        D6(i,j)=AD_1p(i,j);
        F6(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C6(i,j)=AD_2d(i,j);
        E6(i,j)=AD_2p(i,j);
        G6(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H6(i,j)=AD_4d(i,j);
        I6(i,j)=AD_4p(i,j);
        J6(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R6(i,j)=AD_5d(i,j);
        S6(i,j)=AD_5p(i,j);
        T6(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_polyols=sum(B6)/sum(F6);
AAD_2d_polyols=sum(C6)/sum(G6);
AAD_4d_polyols=sum(H6)/sum(J6);
AAD_5d_polyols=sum(R6)/sum(T6);
AAD_1p_polyols=sum(D6)/sum(F6);
AAD_2p_polyols=sum(E6)/sum(G6);
AAD_4p_polyols=sum(I6)/sum(J6);
AAD_5p_polyols=sum(S6)/sum(T6);

% -- Ethers
v8=[41,51,54,57,59,60,74,92];
for i=v8
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B8(i,j)=AD_1d(i,j);
        D8(i,j)=AD_1p(i,j);
        F8(i,j)=nn_1(i,j);
        end
```

```
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C8(i,j)=AD_2d(i,j);
        E8(i,j)=AD_2p(i,j);
        G8(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H8(i,j)=AD_4d(i,j);
        I8(i,j)=AD_4p(i,j);
        J8(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R8(i,j)=AD_5d(i,j);
        S8(i,j)=AD_5p(i,j);
        T8(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B8(i,j)=AD_1d(i,j);
        D8(i,j)=AD_1p(i,j);
        F8(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0  ...
                && T(i,j)<=C_1(i)
        C8(i,j)=AD_2d(i,j);
        E8(i,j)=AD_2p(i,j);
        G8(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H8(i,j)=AD_4d(i,j);
        I8(i,j)=AD_4p(i,j);
        J8(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R8(i,j)=AD_5d(i,j);
        S8(i,j)=AD_5p(i,j);
        T8(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_ethers=sum(B8)/sum(F8);
```

```
AAD_2d_ethers=sum(C8)/sum(G8);
AAD_4d_ethers=sum(H8)/sum(J8);
AAD_5d_ethers=sum(R8)/sum(T8);
AAD_1p_ethers=sum(D8)/sum(F8);
AAD_2p_ethers=sum(E8)/sum(G8);
AAD_4p_ethers=sum(I8)/sum(J8);
AAD_5p_ethers=sum(S8)/sum(T8);

% -- Ketones
v7=[17,19,20,29,30,36];
for i=v7
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B7(i,j)=AD_1d(i,j);
        D7(i,j)=AD_1p(i,j);
        F7(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C7(i,j)=AD_2d(i,j);
        E7(i,j)=AD_2p(i,j);
        G7(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H7(i,j)=AD_4d(i,j);
        I7(i,j)=AD_4p(i,j);
        J7(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R7(i,j)=AD_5d(i,j);
        S7(i,j)=AD_5p(i,j);
        T7(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B7(i,j)=AD_1d(i,j);
        D7(i,j)=AD_1p(i,j);
        F7(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
```

```
        C7(i,j)=AD_2d(i,j);
        E7(i,j)=AD_2p(i,j);
        G7(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0  && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H7(i,j)=AD_4d(i,j);
        I7(i,j)=AD_4p(i,j);
        J7(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0  && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R7(i,j)=AD_5d(i,j);
        S7(i,j)=AD_5p(i,j);
        T7(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_ketones=sum(B7)/sum(F7);
AAD_2d_ketones=sum(C7)/sum(G7);
AAD_4d_ketones=sum(H7)/sum(J7);
AAD_5d_ketones=sum(R7)/sum(T7);
AAD_1p_ketones=sum(D7)/sum(F7);
AAD_2p_ketones=sum(E7)/sum(G7);
AAD_4p_ketones=sum(I7)/sum(J7);
AAD_5p_ketones=sum(S7)/sum(T7);

% -- Thiols
v9=[70,101,123,154,178];
for i=v9
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0  && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B9(i,j)=AD_1d(i,j);
        D9(i,j)=AD_1p(i,j);
        F9(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0  && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C9(i,j)=AD_2d(i,j);
        E9(i,j)=AD_2p(i,j);
        G9(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0  && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H9(i,j)=AD_4d(i,j);
```

```
            I9(i,j)=AD_4p(i,j);
            J9(i,j)=nn_4(i,j);
            end
            if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                    && T(i,j)<=C_1(i)
            R9(i,j)=AD_5d(i,j);
            S9(i,j)=AD_5p(i,j);
            T9(i,j)=nn_5(i,j);
            end
        end
    elseif k>0.45*Tc(i)/Step
        for j=1:k
            if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                    && T(i,j)<=C_1(i)
            B9(i,j)=AD_1d(i,j);
            D9(i,j)=AD_1p(i,j);
            F9(i,j)=nn_1(i,j);
            end
            if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                    && T(i,j)<=C_1(i)
            C9(i,j)=AD_2d(i,j);
            E9(i,j)=AD_2p(i,j);
            G9(i,j)=nn_2(i,j);
            end
            if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                    && T(i,j)<=C_1(i)
            H9(i,j)=AD_4d(i,j);
            I9(i,j)=AD_4p(i,j);
            J9(i,j)=nn_4(i,j);
            end
            if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                    && T(i,j)<=C_1(i)
            R9(i,j)=AD_5d(i,j);
            S9(i,j)=AD_5p(i,j);
            T9(i,j)=nn_5(i,j);
            end
        end
    end
    end
    AAD_1d_thiols=sum(B9)/sum(F9);
    AAD_2d_thiols=sum(C9)/sum(G9);
    AAD_4d_thiols=sum(H9)/sum(J9);
    AAD_5d_thiols=sum(R9)/sum(T9);
    AAD_1p_thiols=sum(D9)/sum(F9);
    AAD_2p_thiols=sum(E9)/sum(G9);
    AAD_4p_thiols=sum(I9)/sum(J9);
    AAD_5p_thiols=sum(S9)/sum(T9);

    % -- Alkenes
```

```
v10=[17,19,20,29,30,36];
for i=v10
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B10(i,j)=AD_1d(i,j);
        D10(i,j)=AD_1p(i,j);
        F10(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C10(i,j)=AD_2d(i,j);
        E10(i,j)=AD_2p(i,j);
        G10(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H10(i,j)=AD_4d(i,j);
        I10(i,j)=AD_4p(i,j);
        J10(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R10(i,j)=AD_5d(i,j);
        S10(i,j)=AD_5p(i,j);
        T10(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        B10(i,j)=AD_1d(i,j);
        D10(i,j)=AD_1p(i,j);
        F10(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        C10(i,j)=AD_2d(i,j);
        E10(i,j)=AD_2p(i,j);
        G10(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        H10(i,j)=AD_4d(i,j);
        I10(i,j)=AD_4p(i,j);
        J10(i,j)=nn_4(i,j);
```

```
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 ...
                && T(i,j)<=C_1(i)
        R10(i,j)=AD_5d(i,j);
        S10(i,j)=AD_5p(i,j);
        T10(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_alkenes=sum(B10)/sum(F10);
AAD_2d_alkenes=sum(C10)/sum(G10);
AAD_4d_alkenes=sum(H10)/sum(J10);
AAD_5d_alkenes=sum(R10)/sum(T10);
AAD_1p_alkenes=sum(D10)/sum(F10);
AAD_2p_alkenes=sum(E10)/sum(G10);
AAD_4p_alkenes=sum(I10)/sum(J10);
AAD_5p_alkenes=sum(S10)/sum(T10);

% -- Associative
v11=[1,3,4,6,7,8,10,12,13,16,21,28,31,34,36,39,40,44,50,52,53,62,71,76,.
    82,85,87,88,90,95,114,116,117,120,162,165,167,169,173,177,179,180,..
    183,184,185]; % Removed points: 79, 176.
for i=v11
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        B11(i,j)=AD_1d(i,j);
        D11(i,j)=AD_1p(i,j);
        F11(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        C11(i,j)=AD_2d(i,j);
        E11(i,j)=AD_2p(i,j);
        G11(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        H11(i,j)=AD_4d(i,j);
        I11(i,j)=AD_4p(i,j);
        J11(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        R11(i,j)=AD_5d(i,j);
        S11(i,j)=AD_5p(i,j);
```

```
        T11(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        B11(i,j)=AD_1d(i,j);
        D11(i,j)=AD_1p(i,j);
        F11(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        C11(i,j)=AD_2d(i,j);
        E11(i,j)=AD_2p(i,j);
        G11(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        H11(i,j)=AD_4d(i,j);
        I11(i,j)=AD_4p(i,j);
        J11(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        R11(i,j)=AD_5d(i,j);
        S11(i,j)=AD_5p(i,j);
        T11(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_associative=sum(B11)/sum(F11);
AAD_2d_associative=sum(C11)/sum(G11);
AAD_4d_associative=sum(H11)/sum(J11);
AAD_5d_associative=sum(R11)/sum(T11);
AAD_1p_associative=sum(D11)/sum(F11);
AAD_2p_associative=sum(E11)/sum(G11);
AAD_4p_associative=sum(I11)/sum(J11);
AAD_5p_associative=sum(S11)/sum(T11);

% -- Non-associative
v12=[2,5,9,11,14,15,17,18,19,20,22,23,24,25,26,27,29,30,32,33,35,37,38,.
    41,42,43,45,46,47,48,49,51,54,55,56,57,58,59,60,61,63,64,65,66,67,..
    68,69,70,72,73,74,75,77,78,80,81,83,84,86,89,91,92,93,94,96,97,...
    99,101,102,103,105,106,107,110,111,115,...
    118,119,122,123,124,125,126,127,128,129,130,131,132,133,134,...
    135,136,137,138,139,140,141,142,143,144,145,146,147,148,149,150,...
    151,153,154,155,156,157,158,159,160,161,163,164,166,168,170,...
```

```
    171,172,174,175,178,181,182]; % Removed points: 98,100,104,108,109,.
    %112,113,121,152.
for i=v12
    k=round(0.45*Tc(i)/Step,0);
if k <= 0.45*Tc(i)/Step
    for j=1:k+1
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        B12(i,j)=AD_1d(i,j);
        D12(i,j)=AD_1p(i,j);
        F12(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        C12(i,j)=AD_2d(i,j);
        E12(i,j)=AD_2p(i,j);
        G12(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        H12(i,j)=AD_4d(i,j);
        I12(i,j)=AD_4p(i,j);
        J12(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        R12(i,j)=AD_5d(i,j);
        S12(i,j)=AD_5p(i,j);
        T12(i,j)=nn_5(i,j);
        end
    end
elseif k>0.45*Tc(i)/Step
    for j=1:k
        if ERROR_1(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        B12(i,j)=AD_1d(i,j);
        D12(i,j)=AD_1p(i,j);
        F12(i,j)=nn_1(i,j);
        end
        if ERROR_2(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        C12(i,j)=AD_2d(i,j);
        E12(i,j)=AD_2p(i,j);
        G12(i,j)=nn_2(i,j);
        end
        if ERROR_4(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        H12(i,j)=AD_4d(i,j);
        I12(i,j)=AD_4p(i,j);
```

```
        J12(i,j)=nn_4(i,j);
        end
        if ERROR_5(i,j)==0 && Density_3(i,j)>0 && Pressure_3(i,j)>0 &&..
                T(i,j)<= C_1(i)
        R12(i,j)=AD_5d(i,j);
        S12(i,j)=AD_5p(i,j);
        T12(i,j)=nn_5(i,j);
        end
    end
end
end
AAD_1d_nonassociative=sum(B12)/sum(F12);
AAD_2d_nonassociative=sum(C12)/sum(G12);
AAD_4d_nonassociative=sum(H12)/sum(J12);
AAD_5d_nonassociative=sum(R12)/sum(T12);
AAD_1p_nonassociative=sum(D12)/sum(F12);
AAD_2p_nonassociative=sum(E12)/sum(G12);
AAD_4p_nonassociative=sum(I12)/sum(J12);
AAD_5p_nonassociative=sum(S12)/sum(T12);

% Displaying ---------------------------------------------------------
disp('1: Method 1 - Pure CPA EoS')
disp('2: Method 2 - correlated a0 and b')
disp('3: DIPPR data')
disp('4: Method 3 - correlated a0 and b and fitted c1')
disp('5: Method 4 - correlated b and fitted c1 and Gamma')
disp('D - Liquid densities')
disp('P - Vapour pressures')
disp('AAD - Average Absolute Deviation')
disp(' ')
disp('Number of considered points: 1D & 1P, 2D & 2P, 4D & 4P, 5D & 5P')
disp(n_1)
disp(n_2)
disp(n_4)
disp(n_5)

disp('AAD / %: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(AAD_1d)
disp(AAD_2d)
disp(AAD_4d)
disp(AAD_5d)
disp(AAD_1p)
disp(AAD_2p)
disp(AAD_4p)
disp(AAD_5p)

disp('1D: AAD min, idx, AAD max, idx')
disp(Min_1d)
disp(I_1d)
```

```
disp(Max_1d)
disp(I_1dm)
disp('2D: AAD min, idx, AAD max, idx')
disp(Min_2d)
disp(I_2d)
disp(Max_2d)
disp(I_2dm)
disp('4D: AAD min, idx, AAD max, idx')
disp(Min_4d)
disp(I_4d)
disp(Max_4d)
disp(I_4dm)
disp('5D: AAD min, idx, AAD max, idx')
disp(Min_5d)
disp(I_5d)
disp(Max_5d)
disp(I_5dm)
disp('1P: AAD min, idx, AAD max, idx')
disp(Min_1p)
disp(I_1p)
disp(Max_1p)
disp(I_1pm)
disp('2P: AAD min, idx, AAD max, idx')
disp(Min_2p)
disp(I_2p)
disp(Max_2p)
disp(I_2pm)
disp('4P: AAD min, idx, AAD max, idx')
disp(Min_4p)
disp(I_4p)
disp(Max_4p)
disp(I_4pm)
disp('5P: AAD min, idx, AAD max, idx')
disp(Min_5p)
disp(I_5p)
disp(Max_5p)
disp(I_5pm)

disp('Alcohols - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v1))
disp(AAD_1d_alcohols)
disp(AAD_2d_alcohols)
disp(AAD_4d_alcohols)
disp(AAD_5d_alcohols)
disp(AAD_1p_alcohols)
disp(AAD_2p_alcohols)
disp(AAD_4p_alcohols)
disp(AAD_5p_alcohols)
```

```
disp('Alkanes - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v2))
disp(AAD_1d_alkanes)
disp(AAD_2d_alkanes)
disp(AAD_4d_alkanes)
disp(AAD_5d_alkanes)
disp(AAD_1p_alkanes)
disp(AAD_2p_alkanes)
disp(AAD_4p_alkanes)
disp(AAD_5p_alkanes)

disp('Alkenes - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v10))
disp(AAD_1d_alkenes)
disp(AAD_2d_alkenes)
disp(AAD_4d_alkenes)
disp(AAD_5d_alkenes)
disp(AAD_1p_alkenes)
disp(AAD_2p_alkenes)
disp(AAD_4p_alkenes)
disp(AAD_5p_alkenes)

disp('Amines - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v3))
disp(AAD_1d_amines)
disp(AAD_2d_amines)
disp(AAD_4d_amines)
disp(AAD_5d_amines)
disp(AAD_1p_amines)
disp(AAD_2p_amines)
disp(AAD_4p_amines)
disp(AAD_5p_amines)

disp('Aromatics - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v4))
disp(AAD_1d_aromatics)
disp(AAD_2d_aromatics)
disp(AAD_4d_aromatics)
disp(AAD_5d_aromatics)
disp(AAD_1p_aromatics)
disp(AAD_2p_aromatics)
disp(AAD_4p_aromatics)
disp(AAD_5p_aromatics)

disp('Esters - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v5))
disp(AAD_1d_esters)
disp(AAD_2d_esters)
disp(AAD_4d_esters)
```

```
disp(AAD_5d_esters)
disp(AAD_1p_esters)
disp(AAD_2p_esters)
disp(AAD_4p_esters)
disp(AAD_5p_esters)

disp('Ethers - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v8))
disp(AAD_1d_ethers)
disp(AAD_2d_ethers)
disp(AAD_4d_ethers)
disp(AAD_5d_ethers)
disp(AAD_1p_ethers)
disp(AAD_2p_ethers)
disp(AAD_4p_ethers)
disp(AAD_5p_ethers)

disp('Ketones - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v7))
disp(AAD_1d_ketones)
disp(AAD_2d_ketones)
disp(AAD_4d_ketones)
disp(AAD_5d_ketones)
disp(AAD_1p_ketones)
disp(AAD_2p_ketones)
disp(AAD_4p_ketones)
disp(AAD_5p_ketones)

disp('Polyols - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v6))
disp(AAD_1d_polyols)
disp(AAD_2d_polyols)
disp(AAD_4d_polyols)
disp(AAD_5d_polyols)
disp(AAD_1p_polyols)
disp(AAD_2p_polyols)
disp(AAD_4p_polyols)
disp(AAD_5p_polyols)

disp('Thiols - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v9))
disp(AAD_1d_thiols)
disp(AAD_2d_thiols)
disp(AAD_4d_thiols)
disp(AAD_5d_thiols)
disp(AAD_1p_thiols)
disp(AAD_2p_thiols)
disp(AAD_4p_thiols)
disp(AAD_5p_thiols)
```

```
disp('Associative - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v11))
disp(AAD_1d_associative)
disp(AAD_2d_associative)
disp(AAD_4d_associative)
disp(AAD_5d_associative)
disp(AAD_1p_associative)
disp(AAD_2p_associative)
disp(AAD_4p_associative)
disp(AAD_5p_associative)

disp('Non-associative - nr, AAD: 1D, 2D, 4D, 5D, 1P, 2P, 4P, 5P')
disp(length(v12))
disp(AAD_1d_nonassociative)
disp(AAD_2d_nonassociative)
disp(AAD_4d_nonassociative)
disp(AAD_5d_nonassociative)
disp(AAD_1p_nonassociative)
disp(AAD_2p_nonassociative)
disp(AAD_4p_nonassociative)
disp(AAD_5p_nonassociative)

% Plotting -------------------------------------------------------------
% Smallest AAD in Vapour Pressure - Method 4
Step=1;
k=round(0.45*C_1(I_5p)/Step,0);
if k <= 0.45*C_1(I_5p)/Step
    for j=1:k+1
        if ERROR_1(I_5p,j)==0 && ERROR_2(I_5p,j)==0 &&...
                ERROR_4(I_5p,j)==0 && ERROR_5(I_5p,j)==0
        P1_5p(1,j)=Pressure_1(I_5p,j);
        P2_5p(1,j)=Pressure_2(I_5p,j);
        P3_5p(1,j)=Pressure_3(I_5p,j);
        P4_5p(1,j)=Pressure_4(I_5p,j);
        P5_5p(1,j)=Pressure_5(I_5p,j);
        T_5p(1,j)=T(I_5p,j);
        end
    end
elseif k>0.45*C_1(I_5p)/Step
    for j=1:k
       if ERROR_1(I_5p,j)==0 && ERROR_2(I_5p,j)==0 &&...
                ERROR_4(I_5p,j)==0 && ERROR_5(I_5p,j)==0
        P1_5p(1,j)=Pressure_1(I_5p,j);
        P2_5p(1,j)=Pressure_2(I_5p,j);
        P3_5p(1,j)=Pressure_3(I_5p,j);
        P4_5p(1,j)=Pressure_4(I_5p,j);
        P5_5p(1,j)=Pressure_5(I_5p,j);
        T_5p(1,j)=T(I_5p,j);
```

```
        end
    end
end
figure('name','Smallest error in Vapour Pressure - Method 4')
plot(T_5p, P3_5p,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Vapour Pressure / Pa');
hold on
scatter(T_5p, P1_5p,8,'sr','filled');
scatter(T_5p, P2_5p,8, 'vg','filled');
scatter(T_5p, P4_5p,8, 'db','filled');
scatter(T_5p, P5_5p,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'northwest');
hold off

% Smallest AAD in Vapour Pressure - Method 3
k=round(0.45*C_1(I_4p)/Step,0);
if k <= 0.45*C_1(I_4p)/Step
    for j=1:k+1
        if ERROR_1(I_4p,j)==0 && ERROR_2(I_4p,j)==0 &&...
                ERROR_4(I_4p,j)==0 && ERROR_5(I_4p,j)==0
        P1_4p(1,j)=Pressure_1(I_4p,j);
        P2_4p(1,j)=Pressure_2(I_4p,j);
        P3_4p(1,j)=Pressure_3(I_4p,j);
        P4_4p(1,j)=Pressure_4(I_4p,j);
        P5_4p(1,j)=Pressure_5(I_4p,j);
        T_4p(1,j)=T(I_4p,j);
        end
    end
elseif k>0.45*C_1(I_4p)/Step
    for j=1:k
       if ERROR_1(I_4p,j)==0 && ERROR_2(I_4p,j)==0 &&...
                ERROR_4(I_4p,j)==0 && ERROR_5(I_4p,j)==0
        P1_4p(1,j)=Pressure_1(I_4p,j);
        P2_4p(1,j)=Pressure_2(I_4p,j);
        P3_4p(1,j)=Pressure_3(I_4p,j);
        P4_4p(1,j)=Pressure_4(I_4p,j);
        P5_4p(1,j)=Pressure_5(I_4p,j);
        T_4p(1,j)=T(I_4p,j);
        end
    end
end
figure('name','Smallest error in Vapour Pressure - Method 3')
plot(T_4p, P3_4p,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Vapour Pressure / Pa');
hold on
scatter(T_4p, P1_4p,8,'sr','filled');
```

```
scatter(T_4p, P2_4p,8, 'vg','filled');
scatter(T_4p, P4_4p,8, 'db','filled');
scatter(T_4p, P5_4p,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'northwest');
hold off

% Smallest error in Vapour Pressure - Method 2
k=round(0.45*C_1(I_2p)/Step,0);
if k <= 0.45*C_1(I_2p)/Step
    for j=1:k+1
        if ERROR_1(I_2p,j)==0 && ERROR_2(I_2p,j)==0 &&...
                ERROR_4(I_2p,j)==0 && ERROR_5(I_2p,j)==0
        P1_2p(1,j)=Pressure_1(I_2p,j);
        P2_2p(1,j)=Pressure_2(I_2p,j);
        P3_2p(1,j)=Pressure_3(I_2p,j);
        P4_2p(1,j)=Pressure_4(I_2p,j);
        P5_2p(1,j)=Pressure_5(I_2p,j);
        T_2p(1,j)=T(I_2p,j);
        end
    end
elseif k>0.45*C_1(I_2p)/Step
    for j=1:k
        if ERROR_1(I_2p,j)==0 && ERROR_2(I_2p,j)==0 &&...
                ERROR_4(I_2p,j)==0 && ERROR_5(I_2p,j)==0
        P1_2p(1,j)=Pressure_1(I_2p,j);
        P2_2p(1,j)=Pressure_2(I_2p,j);
        P3_2p(1,j)=Pressure_3(I_2p,j);
        P4_2p(1,j)=Pressure_4(I_2p,j);
        P5_2p(1,j)=Pressure_5(I_2p,j);
        T_2p(1,j)=T(I_2p,j);
        end
    end
end
figure('name','Smallest error in Vapour Pressure - Method 2')
plot(T_2p, P3_2p,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Vapour Pressure / Pa');
hold on
scatter(T_2p, P1_2p,8,'sr','filled');
scatter(T_2p, P2_2p,8, 'vg','filled');
scatter(T_2p, P4_2p,8, 'db','filled');
scatter(T_2p, P5_2p,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'northwest');
hold off

% Smallest error in Vapour Pressure - Method 1
k=round(0.45*C_1(I_1p)/Step,0);
```

```
if k <= 0.45*C_1(I_1p)/Step
    for j=1:k+1
        if ERROR_1(I_1p,j)==0 && ERROR_2(I_1p,j)==0 &&...
                ERROR_4(I_1p,j)==0 && ERROR_5(I_1p,j)==0
        P1_1p(1,j)=Pressure_1(I_1p,j);
        P2_1p(1,j)=Pressure_2(I_1p,j);
        P3_1p(1,j)=Pressure_3(I_1p,j);
        P4_1p(1,j)=Pressure_4(I_1p,j);
        P5_1p(1,j)=Pressure_5(I_1p,j);
        T_1p(1,j)=T(I_1p,j);
        end
    end
elseif k>0.45*C_1(I_1p)/Step
    for j=1:k
        if ERROR_1(I_1p,j)==0 && ERROR_2(I_1p,j)==0 &&...
                ERROR_4(I_1p,j)==0 && ERROR_5(I_1p,j)==0
        P1_1p(1,j)=Pressure_1(I_1p,j);
        P2_1p(1,j)=Pressure_2(I_1p,j);
        P3_1p(1,j)=Pressure_3(I_1p,j);
        P4_1p(1,j)=Pressure_4(I_1p,j);
        P5_1p(1,j)=Pressure_5(I_1p,j);
        T_1p(1,j)=T(I_1p,j);
        end
    end
end
figure('name','Smallest error in Vapour Pressure - CPA EoS')
plot(T_1p, P3_1p,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Vapour Pressure / Pa');
hold on
scatter(T_1p, P1_1p,8,'sr','filled');
scatter(T_1p, P2_1p,8, 'vg','filled');
scatter(T_1p, P4_1p,8, 'db','filled');
scatter(T_1p, P5_1p,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'northwest');
hold off

% Smallest AAD in Liquid Density - Method 4
k=round(0.45*C_1(I_5d)/Step,0);
if k <= 0.45*C_1(I_5d)/Step
    for j=1:k+1
        if ERROR_1(I_5d,j)==0 && ERROR_2(I_5d,j)==0 &&...
                ERROR_4(I_5d,j)==0 && ERROR_5(I_5d,j)==0
        D1_5d(1,j)=Density_1(I_5d,j);
        D2_5d(1,j)=Density_2(I_5d,j);
        D3_5d(1,j)=Density_3(I_5d,j);
        D4_5d(1,j)=Density_4(I_5d,j);
        D5_5d(1,j)=Density_5(I_5d,j);
```

```
        T_5d(1,j)=T(I_5d,j);
        end
    end
elseif k>0.45*C_1(I_5d)/Step
    for j=1:k
        if ERROR_1(I_5d,j)==0 && ERROR_2(I_5d,j)==0 &&...
                ERROR_4(I_5d,j)==0 && ERROR_5(I_5d,j)==0
        D1_5d(1,j)=Density_1(I_5d,j);
        D2_5d(1,j)=Density_2(I_5d,j);
        D3_5d(1,j)=Density_3(I_5d,j);
        D4_5d(1,j)=Density_4(I_5d,j);
        D5_5d(1,j)=Density_5(I_5d,j);
        T_5d(1,j)=T(I_5d,j);
        end
    end
end
figure('name','Smallest AAD in Liquid Density - Method 4')
plot(T_5d, D3_5d,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Density / kg/m3');
hold on
scatter(T_5d, D1_5d,8, 'sr','filled');
scatter(T_5d, D2_5d,8, 'vg','filled');
scatter(T_5d, D4_5d,8, 'db','filled');
scatter(T_5d, D5_5d,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'southwest');
hold off

% Smallest AAD in Liquid Density - Method 3
k=round(0.45*C_1(I_4d)/Step,0);
if k <= 0.45*C_1(I_4d)/Step
    for j=1:k+1
        if ERROR_1(I_4d,j)==0 && ERROR_2(I_4d,j)==0 &&...
                ERROR_4(I_4d,j)==0 && ERROR_5(I_4d,j)==0
        D1_4d(1,j)=Density_1(I_4d,j);
        D2_4d(1,j)=Density_2(I_4d,j);
        D3_4d(1,j)=Density_3(I_4d,j);
        D4_4d(1,j)=Density_4(I_4d,j);
        D5_4d(1,j)=Density_5(I_4d,j);
        T_4d(1,j)=T(I_4d,j);
        end
    end
elseif k>0.45*C_1(I_4d)/Step
    for j=1:k
        if ERROR_1(I_4d,j)==0 && ERROR_2(I_4d,j)==0 &&...
                ERROR_4(I_4d,j)==0 && ERROR_5(I_4d,j)==0
        D1_4d(1,j)=Density_1(I_4d,j);
        D2_4d(1,j)=Density_2(I_4d,j);
```

```
            D3_4d(1,j)=Density_3(I_4d,j);
            D4_4d(1,j)=Density_4(I_4d,j);
            D5_4d(1,j)=Density_5(I_4d,j);
            T_4d(1,j)=T(I_4d,j);
            end
        end
    end
    figure('name','Smallest AAD in Liquid Density - Method 3')
    plot(T_4d, D3_4d,'k','LineWidth', 3);
    xlabel('Temperature / K');
    ylabel('Density / kg/m3');
    hold on
    scatter(T_4d, D1_4d,8, 'sr','filled');
    scatter(T_4d, D2_4d,8, 'vg','filled');
    scatter(T_4d, D4_4d,8, 'db','filled');
    scatter(T_4d, D5_4d,8, '^m','filled');
    legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
        'southwest');
    hold off

    % Smallest AAD in Liquid Density - Method 2
    k=round(0.45*C_1(I_2d)/Step,0);
    if k <= 0.45*C_1(I_2d)/Step
        for j=1:k+1
            if ERROR_1(I_2d,j)==0 && ERROR_2(I_2d,j)==0 &&...
                    ERROR_4(I_2d,j)==0 && ERROR_5(I_2d,j)==0
            D1_2d(1,j)=Density_1(I_2d,j);
            D2_2d(1,j)=Density_2(I_2d,j);
            D3_2d(1,j)=Density_3(I_2d,j);
            D4_2d(1,j)=Density_4(I_2d,j);
            D5_2d(1,j)=Density_5(I_2d,j);
            T_2d(1,j)=T(I_2d,j);
            end
        end
    elseif k>0.45*C_1(I_2d)/Step
        for j=1:k
            if ERROR_1(I_2d,j)==0 && ERROR_2(I_2d,j)==0 &&...
                    ERROR_4(I_2d,j)==0 && ERROR_5(I_2d,j)==0
            D1_2d(1,j)=Density_1(I_2d,j);
            D2_2d(1,j)=Density_2(I_2d,j);
            D3_2d(1,j)=Density_3(I_2d,j);
            D4_2d(1,j)=Density_4(I_2d,j);
            D5_2d(1,j)=Density_5(I_2d,j);
            T_2d(1,j)=T(I_2d,j);
            end
        end
    end
    figure('name','Smallest AAD in Liquid Density - Method 2')
    plot(T_2d, D3_2d,'k','LineWidth', 3);
```

```
xlabel('Temperature / K');
ylabel('Density / kg/m3');
hold on
scatter(T_2d, D1_2d,8, 'sr','filled');
scatter(T_2d, D2_2d,8, 'vg','filled');
scatter(T_2d, D4_2d,8, 'db','filled');
scatter(T_2d, D5_2d,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'southwest');
hold off

% Smallest error in Liquid Density - Method 1
k=round(0.45*C_1(I_1d)/Step,0);
if k <= 0.45*C_1(I_1d)/Step
    for j=1:k+1
        if ERROR_1(I_1d,j)==0 && ERROR_2(I_1d,j)==0 &&...
                ERROR_5(I_1d,j)==0 && ERROR_5(I_1d,j)==0
        D1_1d(1,j)=Density_1(I_1d,j);
        D2_1d(1,j)=Density_2(I_1d,j);
        D3_1d(1,j)=Density_3(I_1d,j);
        D4_1d(1,j)=Density_4(I_1d,j);
        D5_1d(1,j)=Density_5(I_1d,j);
        T_1d(1,j)=T(I_1d,j);
        end
    end
elseif k>0.45*C_1(I_1d)/Step
    for j=1:k
         if ERROR_1(I_1d,j)==0 && ERROR_2(I_1d,j)==0 &&...
                ERROR_d(I_1d,j)==0 && ERROR_5(I_1d,j)==0
        D1_1d(1,j)=Density_1(I_1d,j);
        D2_1d(1,j)=Density_2(I_1d,j);
        D3_1d(1,j)=Density_3(I_1d,j);
        D4_1d(1,j)=Density_4(I_1d,j);
        D5_1d(1,j)=Density_5(I_1d,j);
        T_1d(1,j)=T(I_1d,j);
        end
    end
end
figure('name','Smallest error in Liquid Density - CPA EoS')
plot(T_1d, D3_1d,'k','LineWidth', 3);
xlabel('Temperature / K');
ylabel('Density / kg/m3');
hold on
scatter(T_1d, D1_1d,8,'sr','filled');
scatter(T_1d, D2_1d,8, 'vg','filled');
scatter(T_1d, D4_1d,8, 'db','filled');
scatter(T_1d, D5_1d,8, '^m','filled');
legend('DIPPR','CPA EoS', 'Method 2','Method 3','Method 4','Location',..
    'southwest');
```

```
hold off

% Comparing the CPA parameters
% Co-volume
for i=[98,100,104,108,109,112,113,121,152]
    b(i)=0;
    a0(i)=0;
    Gamma(i)=0;
end % Compound not found in the DIPPR datbase.
figure('name','Co-volume')
scatter(nonzeros(b), nonzeros(b_2),'k','filled');
xlabel('b / cm3.mol-1');
ylabel('Correlated b / cm3.mol-1');

% Energy parameter
figure('name','Energy parameter')
scatter(nonzeros(a0), nonzeros(a0_2),'g','filled');
xlabel('a0 / bar.L2.mol-2');
ylabel('Correlated a0 / bar.L2.mol-2');

% Corrected energy term parameter
figure('name','Corrected energy term parameter')
scatter(nonzeros(Gamma), nonzeros(Gamma_2),'sb','filled');
xlabel('Gamma / K');
ylabel('Correlated Gamma / K');

% Critical temperature's length adjustment.
Tc_2(79)=0;
Tc_2(98)=0;
Tc_2(100)=0;
Tc_2(104)=0;
Tc_2(108)=0;
Tc_2(109)=0;
Tc_2(112)=0;
Tc_2(113)=0;
Tc_2(121)=0;
Tc_2(152)=0;
Tc_2(176)=0;
figure('name','Critical Temperature')
scatter(nonzeros(Tc_2), nonzeros(C_1),'^r','filled');
xlabel('Tc / K');
ylabel('Tc DIPPR / K');

% Plotting deviations in Vapour Pressure
MW_2=zeros(1,185);
for i=1:NC_t
    if C_1(i)>0
        MW_2(i)=MW(i);
    end
```

```
end
figure('name','Deviations in Vapour Pressure')
scatter(MW_2, rowMean_4p,18, 'sr','filled');
xlabel('Molecular weight / g/mol');
ylabel('Average Absolute Deviation / %');
hold on
scatter(MW_2, rowMean_5p,16, 'ob','filled');
legend('Method 3','Method 4','Location','northeast');
hold off

% Plotting deviations in Liquid Density
figure('name','Deviations in Liquid Density')
scatter(MW_2, rowMean_4d,18, 'sr','filled');
xlabel('Molecular weight / g/mol');
ylabel('Average Absolute Deviation / %');
hold on
scatter(MW_2, rowMean_5d,16, 'ob','filled');
legend('Method 3','Method 4','Location','northeast');
hold off
end
```

G.2 Binary mixtures

```
function HM_Velho

% First things first
    clc;
    clear all %#ok<*CLALL>
    close all
    format long g
    NC_t=197;
    NC_pairs=219;

% Compounds' data -------------------------------------------------------
a0_1=[13.836,11.7176517818393,56.8031490997851,55.2030664405246,15.6949,
    54.5379516930482,46.5815903645002,71.756,35.73856568,...
    27.178511402827,21.983,50.2027971178307,41.582,33.63,22.7576,...
    11.9102,32.1660957141895,33.3033,17.31577733,18.1612,18.9939,...
    33.6294,27.9298,18.3137315,34.1842,28.327,21.218440508304,...
    12.9101198526289,12.2366795100879,23.246503,38.4586,39.8656,...
    22.5775,10.6019,23.0442792132632,38.2621205324426,9.1196,...
    23.31410094,7.86473793864429,27.836,17.87699151715,31.822,...
    29.141,19.260947,10.2546396731511,16.6777,16.832281,...
    41.2962916122326,3.52103834970997,6.37788278775593,...
    8.43804,21.2581800564567,20.942,16.4025,17.246,26.408,...
    24.33523498,17.5724,19.6341041430154,8.43541,12.6295827210537,...
    26.3836,26.38364387,5.5092547452125,8.67166,28.86,29.441,70.4,...
    83.11,18.88,104.7,33.187,12.4190385098894,5.6336,57.73,23.093,...
    21.76523995,90.7,9.0567,28.8616050986152,32.3264,22.8,21.8,...
    55.3253736515302,4.38531429936473,3.8605,28.0789179659996,...
    35.614137,16.890366,12.9094,18.31373,28.4125750886378,...
    2.32037634211438,4.0531,8.57941718957359,21.4505,23.307,...
    59,21.659,74.363,14.5934893,40.53,105.049,34.6,8.23431050317538,...
    22.2695,10.52239108,55.53,122.585,47.06,107,96.06,29.51,18.484,...
    87.973,78.41,66.8,5.4886,26.450466116287,12.139693040266,10.819,...
    29.086,13.14274,29.2373242,40.366,29.237,21.9445901166313,24.015,...
    76.29,138.44,46.66,33.9,47.389,149.4139,62.403,247.5542,129.53,...
    140.3519,196.1025,29.178,186.5301,94.914,23.681,302.3949,32.60544,..
    1.37334321474857,216.9089,119.724,41.250611,205.4853,110.81,34.875,.
    175.5994,85.6417701103819,18.198,38.2021253909077,29.9016579607676,.
    52.3029046041388,43.7024340909577,34.379,23.626,16.9251020979425,...
    18.975,28.796,166.65,76.618,226.98,155.9231,55.2201,...
    24.9813868153875,29,1.39,29.2,28.8416006028167,48.4176876231215,...
    86.4047942994779,35.0019399015019,29.0016143729166,...
    18.8410451073402,9.11875,13.2676,34.822936502161,8.0700933102504,...
    29.3166287,18.845285,16.960394,15.972215,54.5564,17.1480454999981,..
    20.1114725766097,48.634,18.801411,23.3763020103301,15.119,19.502531,
    39.126,1.2277];

b_1=[67.5,64.613,79.7,184.41,173.33,221.37,131.33,110.8,102,148.5,137.8,
    97.455,64.11,139.07,141.199,81.1,77.4,72.8,127.1,109.7,81.05,...
    141.885,124.72,90.4,74.7,69.072,87.74,145.8,144,93,64.11,106.31,...
```

```
    157.43,46.8,87.28,59.2,93.2,74.99,101.65,97.3,76.77,42.59,75.8,...
    84.09,144.4,27.3,40.053,41.41,90.38,94.35,82.4,85.7,92.1,115.78,...
    73.1,76.6,49.6,58.9,115.8,115.78,42.9,49.11,108.7,116,215.6,248.6,..
    83.38,317.8,133.2,58.6,30,182.7,99.3,100.34,282.1,53.1,108.72,...
    124.584,70.6,180.22,29.21,29.2,116.31,101.82,76.97,74.7,81.05,...
    97.54,29.1,30.978,43.82,97.9,98.3,202.8,111.45,240.2,66.25,147.3,...
    315.5,131,43.7,92.6,50.06,179.6,351.8,164.6,333.9,278.3,114.7,81.9,.
    278.2,245.5,212.6,36.1,108.71,54.58,51.4,108.72,72.081,118.89,...
    150.6,117.9,92.3,99.4,242.5,410.7,169.2,133.1,178.65,412.09,216.24,.
    620.31,374.384,391.89,514.24,125.35,495.01,296.1,107.89,717.66,...
    98.38,26.05,557.78,353.889,160.35,533.5,333.685,142.44,472.98,...
    274.53,91.008,133.9,99.9,76.2,82.8,116.4,453.35,250.53,577.7,432.47,
    197.909,95.83,21.6,108.6,97.23,161.67,80.1,57.834,64.1,126.85,...
    52.9,109.8,71.58,65.42,68.41,135.01,81.487,93.5,166.581,77.9,...
    92.14,66.5,115.95,128.926,14.515];

c1_1=[0.9372,0.69706,0.9784,1.068634,1.0642,0.965,1.01096,0.9805,0.843,.
    1.1486,0.97,0.9358,0.91709,0.87461,0.92763,0.88935,0.8476,0.814,...
    1.021,0.965,0.90354,0.96008,0.8991,0.7561,0.7021,0.71721,0.86376,...
    1.1689,1.0432,0.9127,0.9468,0.79961,0.9439,0.4644,1.03323,0.9951,...
    0.8814,0.7576,1.367,0.7533,0.88853,0.63608,0.8803,0.75803,0.9618,...
    0.7602,0.598077,0.76412,0.74265,1.5743,0.84805,0.8838,0.7991,...
    0.94902,0.8937,0.7992,0.72125,0.7213,0.92963,0.92963,0.58463,...
    0.7369,0.8539,0.9103,1.2163,1.2817,0.94265,1.577,1.0422,0.7221,...
    0.3338,1.1336,1.0334,0.84978,1.4865,0.7382,0.8539,0.82473,1.18,...
    1.0436,0.60051,0.50222,1.03889,0.9411,0.91279,0.7021,0.90354,...
    0.82074,0.44718,0.43102,0.66928,0.88703,0.9974,1.3097,1.3371,1.3768,
    0.87185,1.129,1.5496,1.0853,0.8007,0.91446,0.79622,1.0968,1.5966,...
    1.1552,1.86,1.3268,0.9976,0.967,1.4744,1.3667,1.2451,0.6044,0.77664,
    0.8316,0.6744,0.8681,0.70771,0.97798,1.0704,1.025,0.8916,0.9629,...
    1.1315,1.7166,1.1811,1.1038,1.13243,1.59552,1.19531,1.96495,1.53669,
    1.55978,1.80798,0.9137,1.75615,1.3728,0.8313,1.99279,0.8447,...
    0.49855,1.86409,1.50837,1.04628,1.9331,1.46978,0.99415,1.72818,...
    1.3404,0.79858,1.0333,1.045,0.8398,0.9189,1.0161,1.67916,1.29057,...
    1.89769,1.66798,1.1437,0.896,0.4754,0.88,0.8298,0.9795,0.9087,...
    0.6307,0.6891,0.9117,0.6777,0.86256,0.77061,0.87733,0.75793,1.48450,
    0.96139,0.814,1.59108,0.58312,0.8037,0.74544,0.78212,0.967579,0.6735

Tc_1=[626,425.17,563.05,687,616.4,719.4,631.9,611.35,504.03,652.5,566.6,
    586.15,536.78,543.96,553.5,536.05,535.5,565,611.4,587.61,547.78,...
    559.64,530.37,497.7,408.14,417.9,622,629.8,632.7,561.05,508.3,...
    504.43,590.15,591.95,606,508.2,695,562.16,751,720.15,579,584.15,...
    537.2,524,660.55,304.21,378.8,566.73,536.05,736.6,466.7,496.6,...
    744.6,500.05,557,615.02,400.1,503.04,530.6,530.6,305.32,513.92,...
    617.2,571,649.6,705.9,523.3,795.5,587.9,499.15,588,593.8,546,500.23,
    763.4,456.15,617.2,609.15,766.1,698,363.15,373.53,560.8,516.85,513,.
    408.14,547.78,705.85,190.56,512.64,467,512.74,554.5,686.9,741.9,...
    712,506.55,612.3,762.2,590.5,469.95,566,487.2,655.7,781.1,634.1,764,
    786.5,566.9,530.6,471.2,742.9,699.3,430.05,572.19,671.4,720,617.05,.
```

```
    425.18,563.8,616,563.8,570.1,559,674,764,629,594.6,617.7,787,658,...
    855,768,778,826,540.2,819,723,507.6,874,720,126.2,838,758,594.6,832,
    747,568.7,812,708,469.7,593.7,549.7,536.6,538,568.6,804,693,844,796,
    639,697.55,154.58,630.3,704.65,679.9,694.25,369.83,600.81,638.38,...
    364.9,616.23,619,585,542.15,883.6,506.2,530.01,795,632,591.8,536.4,.
    535.35,769.5,647.29];

Vw_1=[46.76,40.82,52.4,113.8,105.69,134.2,83.09,72.86,64.77,93.32,85.23,
    62.63,42.17,88.69,88.6999,54.58,49.27,42.53,79.96,69.73,52.39,88.71,
    78.48,68.25,47.79,44.29,56.67,96.22,90.19,59.5,44.2,68.25,98.94,...
    33.3,54.0,39.4,60.98,48.4,65.58,68.01,47.40,28.8,49.53,54.9,90.2,...
    19.7,22.5,26.32,61.4,65.08,51.5,55.88,60.7,71.9399,46.24,50.04,...
    31.04,38.14,71.96,71.96,27.34,31.94,69.74,73.23,134.6,155.1,52.77,..
    196,83.45,38.71,22.74,114.2,63.0,61.73,175.5,34.44,69.74,80.69,...
    51.36,110.66,17.89,18.72,73.23,65.9199,49.52,47.79,52.39,65.03,...
    17.05,21.71,28.0,61.73,63.00,124.38,75.0,144.84,42.54,93.7,185.8,...
    83.5,28.48,59.49,32.51,114.2,206.2,103.9,202.7,175.5,73.23,...
    52.77,165.3,155.1,134.6,24.21,90.28,39.04,45.87,70.66,47.80,...
    73.23,93.9,73.23,59.17,63.1999,144.84,236.91,103.92,83.46,...
    109.2,231.9,129.6,334.2,211.5,221.7,283.09,78.49,272.9,170.6,68.26,.
    375.2,62.64,15.98,303.55,201.2,98.95,293.3,191,88.72,262.6,160.3,...
    58.03,83.7,63.0,48.94,52.97,73.23,252.4,150.1,313.8,242.2,119.4,...
    65.03,13.0,70.66,65.03,100.43,53.8,37.57,43.42,79.97,34.08,70.66,...
    45.5,41.79,54.34,82.8,52.38,59.15,109.02,50.58,59.51,43.5,76.03,...
    84.86,12.37]; % From DIADEM Professional / cm3/mol

AW=[6960000000,5880000000,19540000000,21050000000,7630000000,...
    15730000000,14510000000,18430000000,11680000000,10330000000,...
    9110000000,20120000000,13030000000,11810000000,8980000000,...
    6280000000,12520000000,12320000000,7620000000,6400000000,...
    5457500000,10450000000,9100000000,7620000000,12330000000,...
    10980000000,9630000000,6930000000,6710000000,7020000000,...
    13020000000,11590000000,7540000000,6270000000,9630000000,...
    13680000000,4890000000,8240000000,4840000000,7670000000,6000000000,.
    8070000000,8110000000,7700000000,4160000000,5990000000,7910000000,..
    11470000000,3200000000,425000000,4000000000,8100000000,9310000000,..
    8530000000,7930000000,9910000000,11420000000,8040000000,3470000000,.
    5630000000,3855000000,10660000000,11230000000,4240000000,4930000000,
    8770000000,10490000000,18590000000,21290000000,7790000000,...
    26690000000,11830000000,3655000000,6240000000,15890000000,...
    9140000000,9880000000,23990000000,5210000000,8770000000,10790000000,
    7650000000,7860000000,14170000000,2650000000,755000000,10490000000,.
    7937500000,5980000000,6930000000,7620000000,8120000000,2690000000,..
    3580000000,4200000000,9870000000,9140000000,17240000000,10670000000,
    19940000000,6440000000,13190000000,25340000000,11840000000,...
    2305000000,8910000000,4890000000,15890000000,28040000000,...
    14540000000,27507500000,23990000000,10490000000,7790000000,...
    22640000000,21290000000,18590000000,3860000000,9440000000,...
    5900000000,5620000000,8840000000,6940000000,10490000000,13190000000,
```

```
    10490000000,6545000000,8940000000,19940000000,32090000000,...
    14540000000,11840000000,15040000000,31240000000,17740000000,...
    44740000000,28540000000,29890000000,37990000000,10990000000,...
    36640000000,23140000000,9640000000,50140000000,7850000000,...
    1200000000,40690000000,27190000000,13690000000,39340000000,...
    25840000000,12340000000,35290000000,21790000000,8290000000,...
    18400000000,16100000000,23000000000,20700000000,11840000000,...
    9140000000,5005000000,7590000000,10490000000,33940000000,...
    20440000000,42040000000,32590000000,16390000000,8120000000,...
    10890000000,1200000000,8840000000,8120000000,12820000000,...
    20700000000,16100000000,10890000000,6700000000,5590000000,...
    6440000000,10120000000,5060000000,8840000000,5600000000,...
    5850000000,7500000000,10540000000,7820000000,6545000000,...
    20800000000,6700000000,7420000000,6000000000,10640000000,...
    14200000000,3500000000]; % / cm2/mol

MW_1=[76.09,54.0916,74.12,158.28,140.27,186.34,116.88,102.16,84.16,...
    130.23,112.21,88.1482,60.09,114.23,114.23,74.123,72.11,70.0898,...
    114.18,100.161,74.122,114.23,100.2,86.18,58.12,56.106,93.13,...
    130.231,128.21,86.13,60.1,86.18,128.25,60.052,102.09,58.08,...
    106.124,78.11,122.12,108.14,114.96,79.904,72.11,73.14,134.22,...
    44.01,66.075,61.46,84.16,105.14,74.12,73.14,106.12,102.18,90.08,...
    94.19,46.07,62.13,102.17,102.17,30.07,46.07,106.17,116.16,200.32,...
    228.37,88.11,284.48,130.18,62.13,46.03,172.26,102.13,88.15,256.42,..
    45.08,106.17,112.21,92.09,162.27,80.91,34.1,116.16,117.15,72.11,...
    58.12,74.122,108.14,16.04,32.04,94.94,88.15,102.13,186.24,119.163,..
    214.24,74.08,144.21,270.24,130.18,48.11,100.121,60.05,172.24,298.24,
    158.24,296.5,256.24,116.16,88.11,242.24,228.24,200.24,31.05,98.186,.
    61.08,62.07,106.16,58.12,116.16,144.21,116.16,90.18,102.13,214.31,..
    340.49,158.23,130.18,142.28,310.6,170.33,450.9,282.55,296.6,380.7,..
    100.21,366.7,226.41,86.18,507,123.11,28.01,408.8,268.5,128.2,394.8,.
    254.5,114.23,352.7,212.42,72.15,130.13,102.13,76.16,88.11,116.13,...
    338.7,198.39,422.8,324.6,156.31,108.14,32,106.16,108.14,148.24,...
    94.11,44.1,74.08,120.2,42.08,106.16,79.1,90.08,134.965,166.13,...
    74.12,90.18,194.23,88.1,92.14,119.38,101.19,150.17,18.02];

Index_1=[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,
    25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,..
    47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,..
    69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,..
    91,92,93,94,95,96,97,98,99,100,101,102,103,104,105,106,107,108,109,.
    110,111,112,113,114,115,116,117,118,119,120,121,122,123,124,125,126,
    127,128,129,130,131,132,133,134,135,136,137,138,139,140,141,142,143,
    144,145,146,147,148,149,150,151,152,153,154,155,156,157,158,159,160,
    161,162,163,164,165,166,167,168,169,170,171,172,173,174,175,176,177,
    178,179,180,181,182,183,184,185];
% Indeces not considering fluorocarbons and used in CPA_Velho.

Index_2=[1,2,5,6,7,8,9,10,11,13,14,15,16,17,18,19,20,21,22,23,24,25,26,.
```

```
    27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,..
    49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,..
    71,72,73,74,75,76,77,78,79,80,81,82,84,85,86,87,88,89,90,91,92,93,..
    94,95,96,97,98,99,100,101,102,103,104,105,106,107,108,109,110,111,..
    112,113,114,115,116,117,118,119,120,121,122,123,124,125,126,127,...
    128,129,130,131,132,133,134,135,136,137,138,139,140,141,142,143,...
    144,145,146,147,148,149,150,151,152,153,154,155,160,161,162,163,...
    164,165,166,167,168,169,170,172,173,174,175,179,180,181,182,183,...
    184,185,186,187,188,189,190,191,192,193,194,195,196,197];

Compound1=[1,5,5,5,5,5,8,9,9,13,13,13,13,15,15,16,16,16,16,16,17,...
        19,19,19,34,34,34,34,34,37,37,37,37,37,37,37,37,37,37,37,37,37,.
        37,37,37,37,37,37,39,39,39,39,39,39,39,39,41,41,41,41,41,41,41,.
        46,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,49,.
        49,49,50,50,50,52,52,52,52,53,53,53,55,55,55,55,55,56,56,56,57,.
        57,57,60,60,60,60,63,63,64,64,64,65,65,65,65,65,65,65,65,65,...
        65,65,65,65,70,77,77,79,79,80,80,80,85,86,86,86,86,86,86,90,...
        91,91,91,92,92,92,92,93,93,93,93,93,94,94,94,94,94,94,94,94,94,.
        94,94,94,101,101,105,106,118,118,119,120,120,121,121,121,...
        121,121,121,121,122,123,123,124,124,133,133,133,133,135,135,135,
        140,140,140,140,143,143,146,149,149,152,152,155,155,169,169,170,
        170,172,173,173,180,193,193,196];

Compound2=[140,74,133,143,181,197,197,49,197,133,135,169,197,140,...
        197,49,52,143,181,197,65,52,140,197,37,52,143,181,197,38,41,...
        49,52,54,62,65,70,91,93,94,101,133,135,149,152,169,193,197,52,..
        94,101,106,123,143,155,197,56,65,94,120,121,196,197,49,56,65,68,
        69,70,75,76,86,93,94,100,101,103,105,109,111,115,121,146,172,...
        196,197,56,121,196,65,94,121,197,142,180,181,65,94,140,143,197,.
        140,193,197,123,140,197,65,93,123,197,140,197,86,121,196,79,...
        90,120,135,140,142,143,152,155,166,180,193,197,197,94,197,123,..
        143,121,196,197,197,93,94,121,180,196,197,94,140,143,197,93,...
        133,149,197,94,105,121,196,197,106,123,133,140,143,149,152,155,.
        180,181,193,197,194,197,146,197,123,143,121,140,197,140,143,...
        149,152,180,193,197,197,196,197,140,197,174,179,196,197,170,...
        196,197,181,191,196,197,196,197,197,196,197,196,197,196,197,196,
        197,179,197,197,196,197,197,196,197,197];

kij_value=[0.032,0.0651,0.015,0.012,-0.02,-0.065,-0.013,-0.0012,...
        -0.042,0.033,0.04,0.04,-0.059,0.024,-0.037,0.0583,0.029,0.017,..
        -0.0385,-0.08,-0.017,0.0302,0.0116,-0.115,-0.0854,...
        0.0296666666666667,0.0235,-0.0648,-0.0848571428571429,-0.0385,..
        0.035,0.019,0.0845,0.03984,-0.00732,-0.0176,-0.001185,-0.0037,..
        0.18,-0.0348,-0.03572,0.0408,0.0379,0.043,0.0543333333333333,...
        0.039,0.02,-0.223,0.022,-0.0157953,0.0069,0.0109,0.035,0.019,...
        0.026,-0.13305,0.028,0.022,0.006,0.0062,0.049,0.032,0.0355,...
        -0.2859,0.035,0.0508,0.0381,0.0481,-0.055,0.0299,-0.0414,...
        0.11793,0.0882,0.0266,0.052,-0.0078,0.0653,0.091,0.0715,0.0566,.
        0.058,0.0826,-0.0578,0.0897,0.035,0.1141,0.08,0.1,0.08,0.033,...
```

```
        0.04,0.059,0.051,-0.0875,0.038,-0.0547,-0.13,-0.162,-0.0025,...
        -0.0005,-0.2914,0.065,0.046,-0.238,0.0069,0.0023,-0.2236,0.1622,
        -0.0032,-0.0374,-0.3044,0.0081,-0.177,0.0847,0.1451,0.135,...
        0.1594,0.018,-0.03,-0.031,0.024,-0.04,0.01,-0.017,0.045,...
        -0.033,0.038,0.014,-0.11,-0.2128,-0.0994,-0.1914,0.0235,0.0125,.
        0.013,0.05,-0.0165,-0.409,0.076,0.022,-0.0253,0.0917,...
        -0.066,-0.098,0.048,0.005,0.0237,-0.06,-0.034,0.0017,0.0062,...
        -0.05,0.01,0.079,0.1563,0.203725913130974,0.1913,0.054,0.048,...
        -0.01,0.005,0.01,-0.006,0.000,0.051,0.05067,0.0008,0.000000,...
        -0.0708181818181818,-0.057,-0.2352,0.159,-0.0695,0.02687,0.0085,
        0.061,0.0145,-0.165,0.047,0.059,0.015,-0.0003,0.11324,...
        0.051,-0.0466,-0.0165,0.113,0.0875,0.04086,-0.2054,-0.072,-0.3,.
        0.08,-0.0658,-0.072,0.073,-0.1205,0.021,0.088,0.09933,0.0095,...
        0.07,0.0355,-0.2,0.09,-0.0425,0.097,-0.0165,0.105,0.0615,0.076,.
        -0.0945,-0.05,-0.115,0.4255,0.05,-0.0165,0.1135,0.037,0.0095,...
        -0.2472];

% Checking the data.
    if length(Compound1)==length(Compound2) &&...
            length(Compound2)==length(kij_value)
        m=length(Compound1);
    else
        disp('WRONG INPUT DIMENSIONS')
        return
    end

% Creating the theorical kij array.
    kij=zeros(NC_t,NC_t);
    for i=1:m
        v1=Compound1(i);
        v2=Compound2(i);
        kij(v1,v2)=kij_value(i);
    end

I=[0,0,0,0,10.06,0,9.42,0,9.84,9.89,9.44,0,0,9.43,10,10.22,9.86,0,...
        9.88,9.38,9.73,9.3,9.35,10.12,9.84,0,10.12,10.57,9.239,9.02,0,..
        9.4,9.38,10.12,10.08,0,10.6547138183364,10,9.705,9.49,9.2459,...
        9.47,8.5,0,11.814,9.84,8.71655089612928,8.69,13.773,11.1736,...
        12.34, 9.86,0,9.51,8.01176437896306,0,9.2,10.5,7.4,10.025,8.69,.
        9.27,9.27,11.52,10.47,8.77,0,0,0,10.01,0,0,9.28659881442548,...
        10.6132557879148,0,10,9.45,0,8.86165400260468,8.77,9.54,0,9.906,
        0,11.66,10.453,0,7.761,9.705,10.57,10.09,8.29,12.51,10.85,10.54,
        9.54,10.0639368848294,0,0,0,10.2712270369371,0,0,0,...
        9.44206642850627,9.7,10.8101814324172,0,0,0,0,0,10.4,10.15,...
        10.4474236662287,0,0,8.97566358626392,9.64,8.96,10.16,8.56,...
        10.53,10,0,10,9.14,10.5,0,0,0,0,9.65,0,0,0,0,0,0,9.92,0,0,...
        10.13,0,9.86,15.5808,0,0,9.72,0,0,9.82,0,0,10.35,0,0,0,0,0,...
        10.04,9.19331824597701,10.52,0,0,0,0,0,9.56,8.14,9.9,12.071,...
        8.56,8.13,0,0,0,9.9,8.47,10.95,10.5199752194664,8.72,9.73,8.44,.
```

```
        9.25,10.3,12.05,9.86,9.97,9.03,0,8.47,8.82,11.37,...
        7.49353899869378,0,12.621]; % Ionisation potential / eV

% Converting the indices in the CPA EoS parameters.
    a0=zeros(1,NC_t);
    b=zeros(1,NC_t);
    c1=zeros(1,NC_t);
    Tc=zeros(1,NC_t);
    Vw=zeros(1,NC_t);
    MW=zeros(1,NC_t);

    for i=1:185
    a0(Index_2(i))=a0_1(Index_1(i));
    b(Index_2(i))=b_1(Index_1(i));
    c1(Index_2(i))=c1_1(Index_1(i));
    Tc(Index_2(i))=Tc_1(Index_1(i));
    Vw(Index_2(i))=Vw_1(Index_1(i));
    MW(Index_2(i))=MW_1(Index_1(i));
    end

% Families
    Alcohols=[5,6,8,9,10,13,15,16,19,24,31,34,65,91,94,189];

    Alkanes=[17,18,25,26,27,28,35,36,64,90,93,123,133,134,135,136,137,..
        138,139,140,141,142,143,144,147,148,149,150,151,152,153,154,155,
        165,166,167,168,169,180];

    Alkenes=[2,7,11,14,29,183];

    Amines=[30,47,53,55,79,99,118,120,185,195];

    Aromatics=[40,41,42,43,48,66,80,84,88,92,122,145,170,173,174,175,...
        179,182,184,188,193];

    Aromatics_HC=[41,48,66,80,84,122,173,175,182,184,195];

    Aromatics_Polar=[40,42,43,88,92,145,170,174,179,188];

    Associative=[1,5,6,8,9,10,13,15,16,19,24,31,34,37,39,42,43,47,55,56,
        65,74,79,82,86,89,91,92,94,99,118,120,124,170,174,179,181,185,..
        188,189,191,192,195,196,197];

    BTEX=[41,93,66,122,173,184]; % With o,p,m-xylene

    Carboxylics=[37,181];

    Esters=[58,67,68,69,70,71,72,74,75,76,78,87,97,98,100,101,102,103,..
        104,106,107,108,109,110,111,112,113,114,115,116,117,124,125,126,
        128,129,130,131,132,160,161,163,164];
```

```
    Ethers=[44,54,57,60,62,63,77,95];

    Glycols=[1,56,121,191];

    Hydrocarbons=[17,18,25,26,27,28,35,36,64,90,93,123,133,134,135,136,.
        137,138,139,140,141,142,143,144,147,148,149,150,151,152,153,154,
        155,165,166,167,168,169,180,2,7,11,14,29,183,41,48,66,80,84,122,
        173,175,182,184,195]; % Alkanes + Alkenes + Aromatics_HC

    Polars=[5,6,8,9,10,13,15,16,19,24,31,34,65,91,94,189,30,47,53,55,79,
        99,118,120,185,195,37,181,58,67,68,69,70,71,72,74,75,76,78,87,..
        97,98,100,101,102,103,104,106,107,108,109,110,111,112,113,114,..
        115,116,117,124,125,126,128,129,130,131,132,160,161,163,164,44,.
        54,57,60,62,63,77,95,1,56,82,121,196,40,42,43,88,92,145,170,174,
        179,188];

    Polyols=[1,56,82,121,196];

    A_1=zeros(1,NC_t);

    for i=1:45
    r=Associative(i);
    A_1(r)=1;
    end
    s=0;
    for i=1:NC_t % Defining the Non-associative vector.
        if A_1(i)==0
            s=s+1;
            Non_associative(s)=i;
        end
    end

% Calculations ---------------------------------------------------------
T=300; % / K
a=zeros(1,NC_t);
for i=1:NC_t % Calculating a.
    if Tc(i)~=0 && a0(i)~=0 && c1(i)~=0
    a(i)=a0(i)*(1+c1(i)*(1-sqrt(T/Tc(i))))^2;
    end
end

bij=zeros(NC_t,NC_t);
for j=1:1:NC_t % Calculating bij.
    for i=1:1:j-1
        if b(i)~=0 && b(j)~=0
            bij(i,j)=0.5*b(i)+0.5*b(j);
        end
    end
```

```
end

% Calculating n in all the compounds, Method 1 -------------------------
nn_1=0;
n_1=zeros(NC_t,NC_t);
kij_calc1x=zeros(NC_t,NC_t);
    for j=1:1:NC_t
        for i=1:1:j-1
            if i<j && abs(kij(i,j))>0 && b(i)>0 && b(j)>0 && I(i)>0 &&..
                    I(j)>0
              nn_1=nn_1+1;
              n_1(i,j)=(log((1-kij(i,j))/(2*sqrt(I(i)*I(j))/...
                  (I(i)+I(j))))/log(sqrt(b(i)*b(j))/bij(i,j))+1)*3;
              kij_calc1x(i,j)=1-2*sqrt(I(i)*I(j))/(I(i)+I(j))*...
                  (sqrt(b(i)*b(j))/bij(i,j))^(n_1(i,j)/3-1);
              AD_1(i,j)=abs((kij_calc1x(i,j)-kij(i,j))/kij(i,j)*100);
            end
        end
    end

    nr_1=0;
    n_1_column=zeros(1,NC_pairs);
    kij_1_column=zeros(1,NC_pairs);
     for i=1:NC_pairs
         nr_1=nr_1+1;
         A=Compound1(i);
         B=Compound2(i);
         n_1_column(nr_1)=n_1(A,B);
         kij_1_column(nr_1)=kij_calc1x(A,B);
     end

     AAD=sum(AD_1,'all')/nn_1;
     disp('Method 1: Considering the ionisation potentials.')
     disp('Method 2: Considering an approximate expression.')
     disp('AAD: Average Absolute Deviations')
     disp('nr: Number of pairs analysed')
     disp(' ')
     disp('All compounds, Method 1: AAD, nr')
     disp(AAD)
     disp(nn_1)
     %disp(n_1_column') %% Displays all n's when active.
     %disp(kij_1_column')  %% Displays all kij's when active.

% Calculating n in all the compounds, Method 2 -------------------------
    nn_2=0;
    n_2=zeros(NC_t,NC_t);
    kij_calc2x=zeros(NC_t,NC_t);
    for j=1:1:NC_t
        for i=1:1:j-1
```

```
            if i<j && abs(kij(i,j))>0 && b(i)>0 && b(j)>0
              nn_2=nn_2+1;
              n_2(i,j)=(log(1-kij(i,j))/log(sqrt(b(i)*b(j))/bij(i,j))+2)
              kij_calc2x(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_2(i,j)/3-2
              AD_2(i,j)=abs((kij_calc2x(i,j)-kij(i,j))/kij(i,j)*100);
            end
        end
    end

    nr_2=0;
    n_2_column=zeros(1,NC_pairs);
    kij_2_column=zeros(1,NC_pairs);
     for i=1:NC_pairs
         nr_2=nr_2+1;
         A=Compound1(i);
         B=Compound2(i);
         n_2_column(nr_2)=n_2(A,B);
         kij_2_column(nr_2)=kij_calc2x(A,B);
     end
     AAD=sum(AD_2,'all')/nn_2;
     disp('All compounds, Method 1: AAD, nr')
     disp(AAD)
     disp(nn_2)
     %disp(n_2_column') %% Displays all n's when active.
     %disp(kij_2_column')  %% Displays all kij's when active.

% Plotting kij and some other properties -------------------------------

% Alkanes and Alcohols
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
```

```
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
figure('name','Alkanes and Alcohols, Method 1')
scatter(b_rat, n_1r, 35, 'og','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Alcohols, Method 1')
scatter(BB_1, n_1r, 35, 'og','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
```

```
% figure('name','Alkanes and Alcohols, Method 1')
% scatter(BB_1, AA_1, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Alcohols, Method 1')
% scatter(b_rat, AA_1, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Alcohols with n < 20
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
```

```
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
figure('name','Alkanes and Alcohols, Method 1 without n > 20')
scatter(b_rat, n_1r, 35, 'og','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Alcohols, Method 1 without n > 20')
scatter(BB_1, n_1r, 35, 'og','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Alcohols, Method 1 without n > 20')
% scatter(BB_1, AA_1, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Alcohols, Method 1 without n > 20')
% scatter(b_rat, AA_1, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat
```

```
% Alkanes and Alcohols with n < 20 with both methods
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
```

```
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            AA_12(nn)=kij_calc2x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            AA_12(nn)=kij_calc2x(i,j);
```

```
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
figure('name','Alkanes and Alcohols, both methods without n > 20')
scatter(b_rat, n_1r, 35, 'og','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
scatter(b_rat2, n_1r2, 35, 'ob','filled');
legend('Method 1','Method 2', 'location','northeast')
hold off

figure('name','Alkanes and Alcohols, both methods without n > 20')
scatter(BB_1, n_1r, 35, 'og','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 35, 'ob','filled');
legend('Method 1','Method 2', 'location','northeast')
hold off

clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2
```

```
% Alkanes and Esters
nn=0;
for j=Alkanes
    for i=Esters
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Esters
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
```

```
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

% figure('name','Alkanes and Esters, Method 1')
% scatter(b_rat, n_1r, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Esters, Method 1')
% scatter(BB_1, n_1r, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Esters, Method 1')
% scatter(BB_1, AA_1, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Esters, Method 1')
% scatter(b_rat, AA_1, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Ethers
nn=0;
for j=Alkanes
    for i=Ethers
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
```

```
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Ethers
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Alkanes and Ethers, Method 1')
% scatter(b_rat, n_1r, 40, 'xr');
```

```
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Ethers, Method 1')
% scatter(BB_1, n_1r, 40, 'xr');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Ethers, Method 1')
% scatter(BB_1, AA_1, 40, 'xr');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Ethers, Method 1')
% scatter(b_rat, AA_1, 40, 'xr');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Polyols
nn=0;
for j=Alkanes
    for i=Polyols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
```

```
            end
        end
    end
end
for j=Polyols
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','Alkanes and Polyols, Method 1')
scatter(b_rat, n_1r, 35, '^m','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Polyols, Method 1')
scatter(BB_1, n_1r, 35, '^m','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Polyols, Method 1')
% scatter(BB_1, AA_1, 35, '^m','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
```

```
% figure('name','Alkanes and Polyols, Method 1')
% scatter(b_rat, AA_1, 35, '^m','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Polyols without n > 20
nn=0;
for j=Alkanes
    for i=Polyols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Polyols
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                I(i)>0 && I(j)>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
```

```
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','Alkanes and Polyols, Method 1 without n > 20')
scatter(b_rat, n_1r, 35, '^m','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Polyols, Method 1 without n > 20')
scatter(BB_1, n_1r, 35, '^m','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Polyols, Method 1 without n > 20')
% scatter(BB_1, AA_1, 35, '^m','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Polyols, Method 1 without n > 20')
% scatter(b_rat, AA_1, 35, '^m','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alcohols and Ethers
nn=0;
for j=Alcohols
    for i=Ethers
```

```
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Ethers
    for i=Alcohols
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(j,i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
```

```
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Alcohols and Ethers, Method 1')
% scatter(b_rat, n_1r, 35, '>b','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alcohols and Ethers, Method 1')
% scatter(BB_1, n_1r, 35, '>b','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alcohols and Ethers, Method 1')
% scatter(BB_1, AA_1, 35, '>b','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alcohols and Ethers, Method 1')
% scatter(b_rat, AA_1, 35, '>b','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Families of compounds with Water -------------------------------------
% Alkanes and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
figure('name','Alkanes and Water, Method 1')
scatter(b_rat, n_1r, 35, '>b','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Water, Method 1')
scatter(BB_1, n_1r, 35, '>b','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Water, Method 1')
scatter(BB_1, AA_1, 35, '>b','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');

figure('name','Alkanes and Water, Method 1')
scatter(b_rat, AA_1, 35, '>b','filled');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Water with n < 20 with both methods
nn=0;
for j=197
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
```

```
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=197
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            AA_12(nn)=kij_calc2x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
```

```
        end
    end
end

figure('name','Alkanes and Water, both methods without n > 20')
scatter(b_rat, n_1r, 35, '>b','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
scatter(b_rat2, n_1r2, 35, '>r','filled');
legend('Method 1','Method 2', 'location','northeast')
hold off

figure('name','Alkanes and Water, both methods without n > 20')
scatter(BB_1, n_1r, 35, '>b','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 35, '>r','filled');
legend('Method 1','Method 2', 'location','northeast')
hold off

clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Amines and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Amines
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
```

```
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Amines and Water, Method 1')
% scatter(b_rat, n_1r, 35, 'om','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Amines and Water, Method 1')
% scatter(BB_1, n_1r, 35, 'om','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Amines and Water, Method 1')
% scatter(BB_1, AA_1, 35, 'om','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Amines and Water, Method 1')
% scatter(b_rat, AA_1, 35, 'om','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Aromatics and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Aromatics
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,compound_idx);
```

```
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Aromatics and Water, Method 1')
% scatter(b_rat, n_1r, 35, 'or','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Aromatics and Water, Method 1')
% scatter(BB_1, n_1r, 35, 'or','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Aromatics and Water, Method 1')
% scatter(BB_1, AA_1, 35, 'or','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Aromatics and Water, Method 1')
% scatter(b_rat, AA_1, 35, 'or','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Ethers and Water
nn=0;
compound_idx=197;
for j=compound_idx
```

```
    for i=Ethers
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,compound_idx);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Ethers and Water, Method 1')
% scatter(b_rat, n_1r, 35, '*b');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Ethers and Water, Method 1')
% scatter(BB_1, n_1r, 35, '*b');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Ethers and Water, Method 1')
% scatter(BB_1, AA_1, 35, '*b');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Ethers and Water, Method 1')
% scatter(b_rat, AA_1, 35, '*b');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
```

```
clear b_rat
clear n_1r

%------------------------------------------------------------------------
% Acetic acid and Alkanes
nn=0;
for j=Alkanes
    for i=37
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
         end
    end
end
for j=37
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
         end
    end
end

nn=0;
for j=Alkanes
    for i=37
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(j)/b(i);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&abs(kij(i,j))>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
         end
    end
end
for j=37
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
```

```
            b_rat2(nn)=b(j)/b(i);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
         end
    end
end
figure('name','Acetic acid and Alkanes, Method 1')
scatter(b_rat, n_1r, 40, '+m');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Acetic acid and Alkanes, Method 1')
scatter(BB_1, n_1r, 40, '+m');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

figure('name','Acetic acid and Alkanes, Method 1')
scatter(BB_1, AA_1, 40, '+m');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');

figure('name','Acetic acid and Alkanes, Method 1')
scatter(b_rat, AA_1, 40, '+m');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');

figure('name','Acetic acid and Alkanes, both methods')
scatter(b_rat, AA_1, 45, 'om');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
hold on
scatter(b_rat2, AA_12, 45, '+k');
legend('Method 1', 'Method 2', 'location', 'northeast')
```

```
hold off

figure('name','Acetic acid and Alkanes, both methods')
scatter(BB_1, AA_1, 45, 'om');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');
hold on
scatter(BB_12, AA_12, 45, '+k');
legend('Method 1', 'Method 2', 'location', 'northeast')
hold off

clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Acetic acid and Alkanes with n < 20 with both methods
nn=0;
for j=37
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
```

```
        end
    end
    for j=Alkanes
        for i=37
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                    I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
                nn=nn+1;
                n_1r(nn)=n_1(i,j);
                AA_1(nn)=kij_calc1x(i,j);
                b_rat(nn)=b(j)/b(i);
                if Vw(i)<Vw(j)
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                    I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
                nn=nn+1;
                n_1r(nn)=n_1(i,j);
                b_rat(nn)=b(i)/b(j);
                AA_1(nn)=kij_calc1x(i,j);
                if Vw(i)<Vw(j)
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end

    nn=0;
    for j=37
        for i=Alkanes
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                    n_2(i,j)<=20
                nn=nn+1;
                n_1r2(nn)=n_2(i,j);
                AA_12(nn)=kij_calc2x(i,j);
                b_rat2(nn)=b(j)/b(i);
                if Vw(i)<Vw(j)
                    BB_12(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_12(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                    abs(kij(i,j))>0 && n_2(i,j)<=20
```

```
                nn=nn+1;
                n_1r2(nn)=n_2(i,j);
                b_rat2(nn)=b(i)/b(j);
                AA_12(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_12(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_12(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end
    for j=Alkanes
        for i=37
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                    n_2(i,j)<=20
                nn=nn+1;
                n_1r2(nn)=n_2(i,j);
                AA_12(nn)=kij_calc2x(i,j);
                b_rat2(nn)=b(j)/b(i);
                if Vw(i)<Vw(j)
                    BB_12(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_12(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                    abs(kij(i,j))>0 && n_2(i,j)<=20
                nn=nn+1;
                n_1r2(nn)=n_2(i,j);
                b_rat2(nn)=b(i)/b(j);
                AA_12(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_12(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_12(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end
    figure('name','Acetic acid and Alkanes, both methods without n > 20')
    scatter(b_rat, n_1r, 45, '+m');
    xlabel('Bigger co-volume ratio');
    ylabel('Calculated exponent');
    hold on
    scatter(b_rat2, n_1r2, 45, '+k');
    legend('Method 1','Method 2', 'location','northeast')
```

```
hold off

figure('name','Acetic acid and Alkanes, both methods without n > 20')
scatter(BB_1, n_1r, 45, '+m');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 45, '+k');
legend('Method 1','Method 2', 'location','northeast')
hold off

clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Butanol and Alkanes
nn=0;
for j=Alkanes
    for i=5
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                 I(i)>0 && I(j)>0&& abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
```

```
        end
    end
    for j=5
        for i=Alkanes
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                     I(i)>0 && I(j)>0
                nn=nn+1;
                n_1r(nn)=n_1(i,j);
                AA_1(nn)=kij_calc1x(i,j);
                b_rat(nn)=b(j)/b(i);
                if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                     I(i)>0 && I(j)>0 && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_1(i,j);
                b_rat(nn)=b(i)/b(j);
                AA_1(nn)=kij_calc1x(i,j);
                if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end
    % figure('name','Butanol and Alkanes, Method 1')
    % scatter(b_rat, n_1r, 35, '<r','filled');
    % xlabel('Bigger co-volume ratio');
    % ylabel('Calculated exponent');
    %
    % figure('name','Butanol and Alkanes, Method 1')
    % scatter(BB_1, n_1r, 35, '<r','filled');
    % xlabel('Bigger van der Waals ratio');
    % ylabel('Calculated exponent');
    %
    % figure('name','Butanol and Alkanes, Method 1')
    % scatter(BB_1, AA_1, 35, '<r','filled');
    % xlabel('Bigger van der Waals ratio');
    % ylabel('Binary Interaction Parameter');
    %
    % figure('name','Butanol and Alkanes, Method 1')
    % scatter(b_rat, AA_1, 35, '<r','filled');
    % xlabel('Bigger co-volume ratio');
```

```
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Carbon dioxide and Alkanes
nn=0;
for j=Alkanes
    for i=49
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=49
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
```

```
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                 I(i)>0 && I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Carbon dioxide and Alkanes, Method 1')
% scatter(b_rat, n_1r, 35, 'oy','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Carbon dioxide and Alkanes, Method 1')
% scatter(BB_1, n_1r, 35, 'oy','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Carbon dioxide and Alkanes, Method 1')
% scatter(BB_1, AA_1, 35, 'oy','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Carbon dioxide and Alkanes, Method 1')
% scatter(b_rat, AA_1, 35, 'oy','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Methanol and Alkanes
nn=0;
for j=Alkanes
    for i=94
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 &&...
                 I(i)>0 && I(j)>0&& abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
```

```
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                 I(i)>0 && I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=94
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                 I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                 I(i)>0 && I(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
        end
    end
end
% figure('name','Methanol and Alkanes, Method 1')
% scatter(b_rat, n_1r, 35, 'sg','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Methanol and Alkanes, Method 1')
% scatter(BB_1, n_1r, 35, 'sg','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Methanol and Alkanes, Method 1')
% scatter(BB_1, AA_1, 35, 'sg','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Methanol and Alkanes, Method 1')
% scatter(b_rat, AA_1, 35, 'sg','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% % Ionisation potential and co-volume ---------------------------------
% % I and all compounds
% nn=0;
% for i=1:1:NC_t
%     if I(i)>0 && b(i)>0 && a(i)>0
%         nn=nn+1;
%         AA_1(nn)=I(i);
%         BB_1(nn)=b(i);
%         CC_1(nn)=Vw(i);
%     end
% end
% figure('name','Ionisation potential and co-volume')
% scatter(BB_1, AA_1, 40, 'ok');
% xlabel('Co-volume / L/mol');
% ylabel('Ionisation potential / eV');
% figure('name','Ionisation potential and van der Waals volume')
% scatter(CC_1, AA_1, 40, 'ob');
% xlabel('Van der Waals volume / cm3/mol');
% ylabel('Ionisation potential / eV');
% clear AA_1
% clear BB_1
% clear CC_1
```

```
%
% % I in alcohols
% nn=0;
% for i=Alcohols
%     if I(i)>0 && b(i)>0 && a(i)>0
%         nn=nn+1;
%         AA_1(nn)=I(i);
%         BB_1(nn)=b(i);
%         CC_1(nn)=Vw(i);
%     end
% end
% figure('name','Ionisation potential in alcohols')
% scatter(BB_1, AA_1, 40, '^k','filled');
% xlabel('Co-volume / L/mol');
% ylabel('Ionisation potential / eV');
% figure('name','Ionisation potential in alcohols')
% scatter(CC_1, AA_1, 40, '^b','filled');
% xlabel('Van der Waals volume / cm3/mol');
% ylabel('Ionisation potential / eV');
% clear AA_1
% clear BB_1
% clear CC_1
%
% % I in alkanes
% nn=0;
% for i=Alkanes
%     if I(i)>0 && b(i)>0 && a(i)>0
%         nn=nn+1;
%         AA_1(nn)=I(i);
%         BB_1(nn)=b(i);
%         CC_1(nn)=Vw(i);
%     end
% end
% figure('name','Ionisation potential in alkanes')
% scatter(BB_1, AA_1, 40, 'ok');
% xlabel('Co-volume / L/mol');
% ylabel('Ionisation potential / eV');
% figure('name','Ionisation potential in alkanes')
% scatter(CC_1, AA_1, 40, 'ob');
% xlabel('Van der Waals volume / cm3/mol');
% ylabel('Ionisation potential / eV');
% clear AA_1
% clear BB_1
% clear CC_1

% % I in ethers
% nn=0;
% for i=Ethers
%     if I(i)>0 && b(i)>0 && a(i)>0
```

```
%         nn=nn+1;
%         AA_1(nn)=I(i);
%         BB_1(nn)=b(i);
%         CC_1(nn)=Vw(i);
%     end
% end
% figure('name','Ionisation potential in ethers')
% scatter(BB_1, AA_1, 40, '*k');
% xlabel('Co-volume / L/mol');
% ylabel('Ionisation potential / eV');
% figure('name','Ionisation potential in ethers')
% scatter(CC_1, AA_1, 40, '*b');
% xlabel('Van der Waals volume / cm3/mol');
% ylabel('Ionisation potential / eV');
% clear AA_1
% clear BB_1
% clear CC_1

% % Method 2 ------------------------------------------------------------
% Alkanes and Alcohols
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            BB_2(nn)=1/BB_1(nn);
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
```

```
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
figure('name','Alkanes and Alcohols, Method 2')
scatter(b_rat, n_1r, 35, 'ob','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Alcohols, Method 2')
scatter(BB_1, n_1r, 35, 'ob','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Alcohols, Method 2')
% scatter(BB_1, AA_1, 35, 'ob','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Alcohols, Method 2')
% scatter(b_rat, AA_1, 35, 'ob','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
```

```
clear b_rat

% Alkanes and Alcohols withou n > 20
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            BB_2(nn)=1/BB_1(nn);
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            BB_2(nn)=1/BB_1(nn);
```

```
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
figure('name','Alkanes and Alcohols, Method 2 without n > 20')
scatter(b_rat, n_1r, 35, 'ob','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Alcohols, Method 2 without n > 20')
scatter(BB_1, n_1r, 35, 'ob','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Alcohols, Method 2 without n > 20')
% scatter(BB_1, AA_1, 35, 'ob','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Alcohols,  Method 2 without n > 20')
% scatter(b_rat, AA_1, 35, 'ob','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Esters
nn=0;
for j=Alkanes
    for i=Esters
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
```

```
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=Esters
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end

% figure('name','Alkanes and Esters, Method 2')
% scatter(b_rat, n_1r, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
```

```
% figure('name','Alkanes and Esters, Method 2')
% scatter(BB_1, n_1r, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Esters, Method 2')
% scatter(BB_1, AA_1, 35, 'og','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Esters, Method 2')
% scatter(b_rat, AA_1, 35, 'og','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Ethers
nn=0;
for j=Alkanes
    for i=Ethers
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=Ethers
```

```
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
% figure('name','Alkanes and Ethers, Method 2')
% scatter(b_rat, n_1r, 35, 'xc');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Ethers, Method 2')
% scatter(BB_1, n_1r, 35, 'xc');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alkanes and Ethers, Method 2')
% scatter(BB_1, AA_1, 35, 'xc');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Ethers, Method 2')
% scatter(b_rat, AA_1, 35, 'xc');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat
```

```
% Alkanes and Polyols
nn=0;
for j=Alkanes
    for i=Polyols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=Polyols
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
```

```
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end

figure('name','Alkanes and Polyols, Method 2')
scatter(b_rat, n_1r, 35, '^c','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Polyols, Method 2')
scatter(BB_1, n_1r, 35, '^c','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Polyols, Method 2')
% scatter(BB_1, AA_1, 35, '^c','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Polyols, Method 2')
% scatter(b_rat, AA_1, 35, '^c','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alkanes and Polyols without n > 20
nn=0;
for j=Alkanes
    for i=Polyols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 && ..
            n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=Polyols
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end

figure('name','Alkanes and Polyols, Method 2 without n > 20')
scatter(b_rat, n_1r, 35, '^c','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
```

```
figure('name','Alkanes and Polyols, Method 2 without n > 20')
scatter(BB_1, n_1r, 35, '^c','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

% figure('name','Alkanes and Polyols, Method 2 without n > 20')
% scatter(BB_1, AA_1, 35, '^c','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alkanes and Polyols, Method 2 without n > 20')
% scatter(b_rat, AA_1, 35, '^c','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Alcohols and Ethers
nn=0;
for j=Alcohols
    for i=Ethers
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
```

```
for j=Ethers
    for i=Alcohols
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(j,i);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
% figure('name','Alcohols and Ethers, Method 2')
% scatter(b_rat, n_1r, 35, '>b','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alcohols and Ethers, Method 2')
% scatter(BB_1, n_1r, 35, '>b','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Alcohols and Ethers, Method 2')
% scatter(BB_1, AA_1, 35, '>b','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Alcohols and Ethers, Method 2')
% scatter(b_rat, AA_1, 35, '>b','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
```

```
clear b_rat

% Families of compounds with Water -------------------------------------
% Alkanes and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end

nn=0;
for j=197
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&..
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(j)/b(i);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
```

```
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
         end
    end
end

figure('name','Alkanes and Water, Method 2')
scatter(b_rat, n_1r, 35, '>r','filled');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Water, Method 2')
scatter(BB_1, n_1r, 35, '>r','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');

figure('name','Alkanes and Water, Method 2')
scatter(BB_1, AA_1, 35, '>r','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');

figure('name','Alkanes and Water, Method 2')
scatter(b_rat, AA_1, 35, '>r','filled');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');

figure('name','Alkanes and Water, both methods')
scatter(BB_12, AA_12, 40, 'ob','filled');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');
hold on
scatter(BB_1, AA_1, 35, '>r','filled');
legend('Method 1', 'Method 2', 'location', 'northeast')
hold off

figure('name','Alkanes and Water, both methods')
scatter(b_rat2, AA_12, 40, 'ob','filled');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
```

```
hold on
scatter(b_rat, AA_1, 35, '>r','filled');
legend('Method 1', 'Method 2', 'location', 'northeast')
hold off
clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Amines and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Amines
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
% figure('name','Amines and Water, Method 2')
% scatter(b_rat, n_1r, 35, 'om','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Amines and Water, Method 2')
```

```
% scatter(BB_1, n_1r, 35, 'om','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Amines and Water, Method 2')
% scatter(BB_1, AA_1, 35, 'om','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Amines and Water, Method 2')
% scatter(b_rat, AA_1, 35, 'om','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Aromatics and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Aromatics
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
% figure('name','Aromatics and Water, Method 2')
```

```
% scatter(b_rat, n_1r, 35, 'or','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Aromatics and Water, Method 2')
% scatter(BB_1, n_1r, 35, 'or','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Aromatics and Water, Method 2')
% scatter(BB_1, AA_1, 35, 'or','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Aromatics and Water, Method 2')
% scatter(b_rat, AA_1, 35, 'or','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Ethers and Water
nn=0;
compound_idx=197;
for j=compound_idx
    for i=Ethers
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,compound_idx);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
```

```
            end
        end
    end
end
% figure('name','Ethers and Water, Method 2')
% scatter(b_rat, n_1r, 35, '*b');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Ethers and Water, Method 2')
% scatter(BB_1, n_1r, 35, '*b');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Ethers and Water, Method 2')
% scatter(BB_1, AA_1, 35, '*b');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Ethers and Water, Method 2')
% scatter(b_rat, AA_1, 35, '*b');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear b_rat
clear n_1r

%-----------------------------------------------------------------------
% Acetic acid and Alkanes
nn=0;
for j=Alkanes
    for i=37
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
```

```
                AA_1(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end
    for j=37
        for i=Alkanes
             if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_2(i,j);
                b_rat(nn)=b(j)/b(i);
                AA_1(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_2(i,j);
                b_rat(nn)=b(i)/b(j);
                AA_1(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_1(nn)=Vw(i)/Vw(j);
                end
             end
        end
    end

    figure('name','Acetic acid and Alkanes, Method 2')
    scatter(b_rat, n_1r, 45, '+k');
    xlabel('Bigger co-volume ratio');
    ylabel('Calculated exponent');

    figure('name','Acetic acid and Alkanes, Method 2')
    scatter(BB_1, n_1r, 45, '+k');
    xlabel('Bigger van der Waals ratio');
    ylabel('Calculated exponent');

    figure('name','Acetic acid and Alkanes, Method 2')
```

```
scatter(BB_1, AA_1, 45, '+k');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');

figure('name','Acetic acid and Alkanes, Method 2')
scatter(b_rat, AA_1, 45, '+k');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Butanol and Alkanes
nn=0;
for j=Alkanes
    for i=5
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=5
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
```

```
                if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_2(i,j);
                b_rat(nn)=b(i)/b(j);
                AA_1(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end
    % figure('name','Butanol and Alkanes, Method 2')
    % scatter(b_rat, n_1r, 35, '<r','filled');
    % xlabel('Bigger co-volume ratio');
    % ylabel('Calculated exponent');
    %
    % figure('name','Butanol and Alkanes, Method 2')
    % scatter(BB_1, n_1r, 35, '<r','filled');
    % xlabel('Bigger van der Waals ratio');
    % ylabel('Calculated exponent');
    %
    % figure('name','Butanol and Alkanes, Method 2')
    % scatter(BB_1, AA_1, 35, '<r','filled');
    % xlabel('Bigger van der Waals ratio');
    % ylabel('Binary Interaction Parameter');
    %
    % figure('name','Butanol and Alkanes, Method 2')
    % scatter(b_rat, AA_1, 35, '<r','filled');
    % xlabel('Bigger co-volume ratio');
    % ylabel('Binary Interaction Parameter');
    clear AA_1
    clear BB_1
    clear n_1r
    clear b_rat

    % Carbon dioxide and Alkanes
    nn=0;
    for j=Alkanes
        for i=49
            if i<j  && b(i)<b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
```

```
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=49
    for i=Alkanes
         if i<j  && b(i)<b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
```

```
    end
end
% figure('name','Carbon dioxide and Alkanes, Method 2')
% scatter(b_rat, n_1r, 35, 'oy','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Carbon dioxide and Alkanes, Method 2')
% scatter(BB_1, n_1r, 35, 'oy','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Carbon dioxide and Alkanes, Method 2')
% scatter(BB_1, AA_1, 35, 'oy','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Carbon dioxide and Alkanes, Method 2')
% scatter(b_rat, AA_1, 35, 'oy','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Methanol and Alkanes
nn=0;
for j=Alkanes
    for i=94
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(i)/b(j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
for j=94
    for i=Alkanes
         if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
% figure('name','Methanol and Alkanes, Method 2')
% scatter(b_rat, n_1r, 35, 'sg','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Calculated exponent');
%
% figure('name','Methanol and Alkanes, Method 2')
% scatter(BB_1, n_1r, 35, 'sg','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Calculated exponent');
%
% figure('name','Methanol and Alkanes, Method 2')
% scatter(BB_1, AA_1, 35, 'sg','filled');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
%
% figure('name','Methanol and Alkanes, Method 2')
```

```
% scatter(b_rat, AA_1, 35, 'sg','filled');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Additional Plots -----------------------------------------------------
% Acetone and Hydrocarbons
nn=0;
for j=Hydrocarbons
    for i=39
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=39
    for i=Hydrocarbons
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
```

```
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=Hydrocarbons
    for i=39
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=39
    for i=Hydrocarbons
```

```
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','Acetone and Hydrocarbons')
scatter(b_rat, n_1r, 45, '*g');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
scatter(b_rat2, n_1r2, 45, 'ok');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','Acetone and Hydrocarbons')
scatter(BB_1, n_1r, 45, '*g');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 45, 'ok');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','Acetone and Hydrocarbons')
scatter(BB_1, AA_1, 45, '*g');
xlabel('Bigger van der Waals ratio');
```

```
ylabel('Binary Interaction Parameter');
hold on
scatter(BB_12, AA_12, 45, 'ok');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','Acetone and Hydrocarbons')
scatter(b_rat, AA_1, 45, '*g');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
hold on
scatter(b_rat2, AA_12, 45, 'ok');
legend('Method 2', 'Method 1', 'location','northeast')
hold off
clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Alkanes and Ethanol
nn=0;
for j=Alkanes
    for i=65
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
```

```
            end
        end
    end

    for j=65
        for i=Alkanes
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_2(i,j);
                AA_1(nn)=kij_calc2x(i,j);
                b_rat(nn)=b(j)/b(i);
                if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
                nn=nn+1;
                n_1r(nn)=n_2(i,j);
                b_rat(nn)=b(i)/b(j);
                AA_1(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_1(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end

    nn=0;
    for j=65
        for i=Alkanes
            if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                    I(i)>0 && I(j)>0
                nn=nn+1;
                n_1r2(nn)=n_1(i,j);
                AA_12(nn)=kij_calc1x(i,j);
                b_rat2(nn)=b(j)/b(i);
                if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_12(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                    BB_12(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                    I(i)>0 && I(j)>0
```

```
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

for j=Alkanes
    for i=65
        if i<j && b(i)<b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0  &&...
                I(i)>0  && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0&&
                I(i)>0  && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','Alkanes and Ethanol')
scatter(b_rat, n_1r, 40, 'or');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
```

```
scatter(b_rat2, n_1r2, 45, 'sk','filled');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','Alkanes and Ethanol')
scatter(BB_1, n_1r, 40, 'or');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 45, 'sk','filled');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

% figure('name','Alkanes and Ethanol')
% scatter(BB_1, AA_1, 40, 'or');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
% hold on
% scatter(BB_12, AA_12, 45, 'sk','filled');
% legend('Method 2', 'Method 1', 'location','northeast')
% hold off
%
% figure('name','Alkanes and Ethanol')
% scatter(b_rat, AA_1, 40, 'or');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
% hold on
% scatter(b_rat2, AA_12, 45, 'sk','filled');
% legend('Method 2', 'Method 1', 'location','northeast')
% hold off
clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% Alkanes and Glycols
nn=0;
for j=Alkanes
    for i=Glycols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
```

```
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

for j=Glycols
    for i=Alkanes
         if i<j  && b(i)<b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j  && b(i)>b(j)  && b(i)>0  && b(j)>0  && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0  && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
```

```
for j=Glycols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

for j=Alkanes
    for i=Glycols
       if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
```

```
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)  && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','Alkanes and Glycols')
scatter(b_rat, n_1r, 45, '*r');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
scatter(b_rat2, n_1r2, 45, 'sb');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','Alkanes and Glycols')
scatter(BB_1, n_1r, 45, '*r');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 45, 'sb');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

% figure('name','Alkanes and Glycols')
% scatter(BB_1, AA_1, 45, '*r');
% xlabel('Bigger van der Waals ratio');
% ylabel('Binary Interaction Parameter');
% hold on
% scatter(BB_12, AA_12, 45, 'sb');
% legend('Method 2', 'Method 1', 'location','northeast')
% hold off
%
% figure('name','Alkanes and Glycols')
% scatter(b_rat, AA_1, 45, '*r');
% xlabel('Bigger co-volume ratio');
% ylabel('Binary Interaction Parameter');
% hold on
% scatter(b_rat2, AA_12, 45, 'sb');
% legend('Method 2', 'Method 1', 'location','northeast')
% hold off
clear AA_1
clear BB_1
clear n_1r
```

```
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% BTEX and Water
nn=0;
for j=197
    for i=BTEX
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            AA_1(nn)=kij_calc2x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=197
    for i=BTEX
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            AA_12(nn)=kij_calc1x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
```

```
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                I(i)>0 && I(j)>0
            nn=nn+1;
            n_1r2(nn)=n_1(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j) && Vw(i)>0 && Vw(j)>0
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

figure('name','BTEX and Water')
scatter(b_rat, n_1r, 45, 'sr');
xlabel('Bigger co-volume ratio');
ylabel('Calculated exponent');
hold on
scatter(b_rat2, n_1r2, 45, '*k');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','BTEX and Water')
scatter(BB_1, n_1r, 45, 'sr');
xlabel('Bigger van der Waals ratio');
ylabel('Calculated exponent');
hold on
scatter(BB_12, n_1r2, 45, '*k');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','BTEX and Water')
scatter(BB_1, AA_1, 45, 'sr');
xlabel('Bigger van der Waals ratio');
ylabel('Binary Interaction Parameter');
hold on
scatter(BB_12, AA_12, 45, '*k');
legend('Method 2', 'Method 1', 'location','northeast')
hold off

figure('name','BTEX and Water')
scatter(b_rat, AA_1, 45, 'sr');
xlabel('Bigger co-volume ratio');
ylabel('Binary Interaction Parameter');
```

```
hold on
scatter(b_rat2, AA_12, 45, '*k');
legend('Method 2', 'Method 1', 'location','northeast')
hold off
clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2

% All compounds together withou n > 20 ---------------------------------
nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
```

```
            n_1r(nn)=n_1(i,j);
            AA_1(nn)=kij_calc1x(i,j);
            b_rat(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r(nn)=n_1(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=Alcohols
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            AA_12(nn)=kij_calc2x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
```

```
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=Alcohols
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            AA_12(nn)=kij_calc2x(i,j);
            b_rat2(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r2(nn)=n_2(i,j);
            b_rat2(nn)=b(i)/b(j);
            AA_12(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_12(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_12(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=197
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r3(nn)=n_1(i,j);
            AA_13(nn)=kij_calc1x(i,j);
            b_rat3(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_13(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
```

```
                BB_13(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r3(nn)=n_1(i,j);
            b_rat3(nn)=b(i)/b(j);
            AA_13(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_13(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_13(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=197
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r4(nn)=n_2(i,j);
            AA_14(nn)=kij_calc2x(i,j);
            b_rat4(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_14(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_14(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r4(nn)=n_2(i,j);
            b_rat4(nn)=b(i)/b(j);
            AA_14(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_14(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_14(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
```

```
nn=0;
for j=37
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r5(nn)=n_1(i,j);
            AA_15(nn)=kij_calc1x(i,j);
            b_rat5(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_15(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_15(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r5(nn)=n_1(i,j);
            b_rat5(nn)=b(i)/b(j);
            AA_15(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_15(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_15(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=37
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r5(nn)=n_1(i,j);
            AA_15(nn)=kij_calc1x(i,j);
            b_rat5(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_15(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_15(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && I(i)>0 &&...
                I(j)>0 && abs(kij(i,j))>0 && n_1(i,j)<=20
            nn=nn+1;
            n_1r5(nn)=n_1(i,j);
            b_rat5(nn)=b(i)/b(j);
```

```
            AA_15(nn)=kij_calc1x(i,j);
            if Vw(i)<Vw(j)
                BB_15(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_15(nn)=Vw(i)/Vw(j);
            end
        end
    end
end

nn=0;
for j=37
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r6(nn)=n_2(i,j);
            AA_16(nn)=kij_calc2x(i,j);
            b_rat6(nn)=b(j)/b(i);
            if Vw(i)<Vw(j)
                BB_16(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_16(nn)=Vw(i)/Vw(j);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                abs(kij(i,j))>0 && n_2(i,j)<=20
            nn=nn+1;
            n_1r6(nn)=n_2(i,j);
            b_rat6(nn)=b(i)/b(j);
            AA_16(nn)=kij_calc2x(i,j);
            if Vw(i)<Vw(j)
                BB_16(nn)=Vw(j)/Vw(i);
            end
            if Vw(i)>Vw(j)
                BB_16(nn)=Vw(i)/Vw(j);
            end
        end
    end
end
for j=Alkanes
    for i=37
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 &&...
                n_2(i,j)<=20
            nn=nn+1;
            n_1r6(nn)=n_2(i,j);
            AA_16(nn)=kij_calc2x(i,j);
            b_rat6(nn)=b(j)/b(i);
```

```
                if Vw(i)<Vw(j)
                    BB_16(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_16(nn)=Vw(i)/Vw(j);
                end
            elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 &&...
                    abs(kij(i,j))>0 && n_2(i,j)<=20
                nn=nn+1;
                n_1r6(nn)=n_2(i,j);
                b_rat6(nn)=b(i)/b(j);
                AA_16(nn)=kij_calc2x(i,j);
                if Vw(i)<Vw(j)
                    BB_16(nn)=Vw(j)/Vw(i);
                end
                if Vw(i)>Vw(j)
                    BB_16(nn)=Vw(i)/Vw(j);
                end
            end
        end
    end

    % Exponent n
    figure('name','Some families, method 1 without n > 20')
    scatter(b_rat, n_1r, 30, 'og','filled');
    xlabel('Bigger co-volume ratio');
    ylabel('Calculated exponent');
    hold on
    scatter(b_rat3, n_1r3, 35, '>b','filled');
    scatter(b_rat5, n_1r5, 45, '+m');
    scatter(b_rat2, n_1r2, 30, 'ob','filled');
    scatter(b_rat4, n_1r4, 35, '>r','filled');
    scatter(b_rat6, n_1r6, 45, '+k');
    legend('Alkanes-Alcohols - Method 1','Alkanes-Water - Method 1',...
        'Acetic acid-Alkanes - Method 1','Alkanes-Alcohols - Method 2',...
        'Alkanes-Water - Method 2','Acetic acid-Alkanes - Method 2',...
        'location','northeast')
    hold off

    figure('name','Some families, method 1 without n > 20')
    scatter(BB_1, n_1r, 30, 'og','filled');
    xlabel('Bigger van der Waals ratio');
    ylabel('Calculated exponent');
    hold on
    scatter(BB_13, n_1r3, 35, '>b','filled');
    scatter(BB_15, n_1r5, 45, '+m');
    scatter(BB_12, n_1r2, 30, 'ob','filled');
    scatter(BB_14, n_1r4, 35, '>r','filled');
    scatter(BB_16, n_1r6, 45, '+k');
```

```
legend('Alkanes-Alcohols - Method 1','Alkanes-Water - Method 1',...
    'Acetic acid-Alkanes - Method 1','Alkanes-Alcohols - Method 2',...
    'Alkanes-Water - Method 2','Acetic acid-Alkanes - Method 2',...
    'location','northeast')
hold off

% Binary interaction parameter
figure('name','Some families, method 1 without n > 20')
scatter(b_rat2, AA_12, 30, 'ob','filled');

xlabel('Bigger co-volume ratio');
ylabel('Binary interaction parameter');
hold on
scatter(b_rat4, AA_14, 35, '>r','filled');
scatter(b_rat6, AA_16, 45, '+k');
scatter(b_rat, AA_1, 30, 'og','filled');
scatter(b_rat3, AA_13, 35, '>b','filled');
scatter(b_rat5, AA_15, 45, '+m');
legend('Alkanes-Alcohols - Method 2','Alkanes-Water - Method 2',...
    'Acetic acid-Alkanes - Method 2','Alkanes-Alcohols - Method 1',...
    'Alkanes-Water - Method 1','Acetic acid-Alkanes - Method 1',...
    'location','northeast')
hold off

figure('name','Some families, method 1 without n > 20')
scatter(BB_12, AA_12, 30, 'ob','filled');

xlabel('Bigger van der Waals ratio');
ylabel('Binary interaction parameter');
hold on
scatter(BB_14, AA_14, 35, '>r','filled');
scatter(BB_16, AA_16, 45, '+k');
scatter(BB_1, AA_1, 30, 'og','filled');
scatter(BB_13, AA_13, 35, '>b','filled');
scatter(BB_15, AA_15, 45, '+m');
legend('Alkanes-Alcohols - Method 2','Alkanes-Water - Method 2',...
    'Acetic acid-Alkanes - Method 2','Alkanes-Alcohols - Method 1',...
    'Alkanes-Water - Method 1','Acetic acid-Alkanes - Method 1',...
    'location','northeast')
hold off

clear AA_1
clear BB_1
clear n_1r
clear b_rat
clear AA_12
clear BB_12
clear n_1r2
clear b_rat2
```

```
clear AA_13
clear BB_13
clear n_1r3
clear b_rat3
clear AA_14
clear BB_14
clear n_1r4
clear b_rat4
clear AA_15
clear BB_15
clear n_1r5
clear b_rat5
clear AA_16
clear BB_16
clear n_1r6
clear b_rat6

% Limits of the model ---------------------------------------------------
nn=0;
for j=2:197
    for i=1:j-1
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0 && ..
                abs(n_2(i,j))<150
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(j)/b(i);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0&&
                abs(n_2(i,j))<150
            nn=nn+1;
            n_1r(nn)=n_2(i,j);
            b_rat(nn)=b(i)/b(j);
            AA_1(nn)=kij_calc2x(i,j);
            if Vw(i)>Vw(j)
                BB_1(nn)=Vw(i)/Vw(j);
            end
            if Vw(i)<Vw(j)
                BB_1(nn)=Vw(j)/Vw(i);
            end
        end
    end
end
```

```
figure('name','Limits of the model')
scatter(b_rat, n_1r, 30, 'oc','filled');
xlim([0 16]);
ylim([-60 140]);
xlabel('Bigger co-volumes ratio');
ylabel('Calculated exponent');
yline(0,'k','linewidth',1);
yline(10,'r','linewidth',1);
xline(1,'-.k','linewidth',1);
xline(2,'-.g','linewidth',1);
legend('Calculated exponents','n = 0','n = 10','b2/b1 = 1','b2/b1 = 2',.
    'location','northeast')

figure('name','Limits of the model')
scatter(BB_1, n_1r, 30, 'ob','filled');
xlim([0 11]);
ylim([-60 140]);
xlabel('Bigger van der Waals volumes ratio');
ylabel('Calculated exponent');
yline(0,'k','linewidth',1);
yline(10,'r','linewidth',1);
xline(1,'-.k','linewidth',1);
xline(2,'-.g','linewidth',1);
legend('Calculated exponents','n = 0','n = 10','b2/b1 = 1','b2/b1 = 2',.
    'location','northeast')
clear AA_1
clear BB_1
clear n_1r
clear b_rat

% Sensitivity analysis -------------------------------------------------
nn=0;
kij_predicted_1=zeros(197,197);
kij_predicted_1_01=zeros(197,197);
kij_predicted_0_99=zeros(197,197);
kij_predicted_1_05=zeros(197,197);
kij_predicted_0_95=zeros(197,197);
kij_predicted_1_10=zeros(197,197);
kij_predicted_0_90=zeros(197,197);
kij_predicted_1_20=zeros(197,197);
kij_predicted_0_80=zeros(197,197);
kij_pc_1=zeros(1,NC_pairs);
kij_pc_1_01=zeros(1,NC_pairs);
kij_pc_0_99=zeros(1,NC_pairs);
kij_pc_1_05=zeros(1,NC_pairs);
kij_pc_0_95=zeros(1,NC_pairs);
kij_pc_1_10=zeros(1,NC_pairs);
kij_pc_0_90=zeros(1,NC_pairs);
kij_pc_1_20=zeros(1,NC_pairs);
```

```
kij_pc_0_80=zeros(1,NC_pairs);
for p=1:NC_pairs
    i=Compound1(p);
    j=Compound2(p);
    nn=nn+1;
    if abs(kij(i,j))>0
kij_predicted_1(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_2(i,j)/3-2);
kij_pc_1(nn)=kij_predicted_1(i,j);

kij_predicted_1_01(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(1.01*n_2(i,j)/3-2)
kij_pc_1_01(nn)=kij_predicted_1_01(i,j);

kij_predicted_0_99(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(0.99*n_2(i,j)/3-2)
kij_pc_0_99(nn)=kij_predicted_0_99(i,j);

kij_predicted_1_05(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(1.05*n_2(i,j)/3-2)
kij_pc_1_05(nn)=kij_predicted_1_05(i,j);

kij_predicted_0_95(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(0.95*n_2(i,j)/3-2)
kij_pc_0_95(nn)=kij_predicted_0_95(i,j);

kij_predicted_0_90(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(0.90*n_2(i,j)/3-2)
kij_pc_0_90(nn)=kij_predicted_0_90(i,j);

kij_predicted_1_10(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(1.10*n_2(i,j)/3-2)
kij_pc_1_10(nn)=kij_predicted_1_10(i,j);

kij_predicted_0_80(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(0.80*n_2(i,j)/3-2)
kij_pc_0_80(nn)=kij_predicted_0_80(i,j);

kij_predicted_1_20(i,j)=1-(sqrt(b(i)*b(j))/bij(i,j))^(1.2*n_2(i,j)/3-2);
kij_pc_1_20(nn)=kij_predicted_1_20(i,j);
    end
end
figure('name','Sensitivity analysis 1')
scatter(kij_2_column, kij_pc_0_95,10,'ob','filled');
xlabel('Theoretical binary interaction parameter');
ylabel('Predicted binary interaction parameter');
hold on
scatter(kij_2_column, kij_pc_0_99, 10, 'oc','filled');
scatter(kij_2_column, kij_pc_1_05, 10, 'or','filled');
scatter(kij_2_column, kij_pc_1_01, 10, 'oy','filled');
scatter(kij_2_column, kij_pc_1,10,'ok','filled');
legend('-5 %', '-1 %', '+5 %', '+1 %', '0 %','location', 'southeast')
hold off

figure('name','Sensitivity analysis 2')
scatter(kij_2_column, kij_pc_0_80,10,'ob','filled');
xlabel('Theoretical binary interaction parameter');
```

```
ylabel('Predicted binary interaction parameter');
hold on
scatter(kij_2_column, kij_pc_0_90, 10, 'oc','filled');
scatter(kij_2_column, kij_pc_1_20, 10, 'or','filled');
scatter(kij_2_column, kij_pc_1_10, 10, 'oy','filled');
scatter(kij_2_column, kij_pc_1,10,'ok','filled');
legend('-20 %', '-10 %', '+20 %', '+10 %', '0 %','location', 'southeast'
hold off

% Alkanes-Water as example
nn=0;
b_rat=zeros(1,11);
kij_predicted=zeros(1,11);
AA_1=zeros(1,11);
n_1r=zeros(NC_t,NC_t);
for j=197
    for i=Alkanes
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(j)/b(i);
            n_1r(i,j)=5.85+5.83*10*exp(-0.838*b(j)/b(i));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(i)/b(j);
            n_1r(i,j)=5.85+5.83*10*exp(-0.838*b(i)/b(j));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        end
    end
end
figure('name','Sensitivity analysis - particular case 1')
scatter(b_rat, kij_predicted,30,'sk','filled');
xlabel('Bigger co-volumes ratio');
ylabel('Binary interaction parameter');
hold on
scatter(b_rat, AA_1,30,'or');
legend('Predicted value','Theoretical value','location','northeast')
hold off

% Acetic acid-Alkanes as example
nn=0;
b_rat=zeros(1,11);
kij_predicted=zeros(1,11);
AA_1=zeros(1,11);
n_1r=zeros(NC_t,NC_t);
for j=37
    for i=Alkanes
```

```
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(j)/b(i);
            n_1r(i,j)=6.45+940*exp(-2.37*b(j)/b(i));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(i)/b(j);
            n_1r(i,j)=6.45+940*exp(-2.37*b(i)/b(j));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        end
    end
end
for j=Alkanes
    for i=37
        if i<j && b(i)<b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(j)/b(i);
            n_1r(i,j)=6.45+940*exp(-2.37*b(j)/b(i));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        elseif i<j && b(i)>b(j) && b(i)>0 && b(j)>0 && abs(kij(i,j))>0
            nn=nn+1;
            b_rat(nn)=b(i)/b(j);
            n_1r(i,j)=6.45+940*exp(-2.37*b(i)/b(j));
            kij_predicted(nn)=1-(sqrt(b(i)*b(j))/bij(i,j))^(n_1r(i,j)/3-
            AA_1(nn)=kij_calc2x(i,j);
        end
    end
end
figure('name','Sensitivity analysis - particular case 2')
scatter(b_rat, kij_predicted,30,'sk','filled');
xlabel('Bigger co-volumes ratio');
ylabel('Binary interaction parameter');
hold on
scatter(b_rat, AA_1,30,'og');
legend('Predicted value','Theoretical value','location','northeast')
hold off
end
```

G.3 Bibliography

[1] G. M. Kontogeorgis, E. C. Voutsas, I. V. Yakoumis and D. P. Tassios. An equation of state for associating fluids. *Industrial & Engineering Chemistry Research*, 35:4310-4318, 1996.

[2] M. L. Michelsen and J. M. Mollerup. *Thermodynamic models: fundamentals & computational aspects*. Tie-line Publications, 2nd edition, 2007. Holte, Denmark.