



**Universidade de Aveiro** Departamento de Química  
**Ano 2014**

**Catarina Ribeiro  
Saraiva**

**ELV e coeficientes de atividade de sistemas de  
Água + Líquidos Iónicos**

**VLE and activity coefficients of ionic liquids +  
water systems**





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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química, realizada sob a orientação científica do Dr. João Manuel da Costa e Araújo Pereira Coutinho, Professor Catedrático do Departamento de Química da Universidade de Aveiro, e coorientação da Dra. Mariana Belo Oliveira, Estagiária de Pós-doutoramento do Departamento de Química da Universidade de Aveiro.



Dedico este trabalho aos meus pais e aos meus irmãos.



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**palavras-chave**

Líquidos iônicos, água, equilíbrio líquido-vapor, coeficientes de atividade da água, soft-SAFT EoS.

**resumo**

A evolução industrial é um fenómeno cada vez mais presente a nível mundial, onde se observa uma elevada procura pela inovação, que se traduz em competitividade e em crescimento. Uma consequência desta inovação está relacionada com a descoberta de um novo tipo de compostos: os líquidos iônicos. Estes têm despertado um elevado interesse nos últimos anos devido às suas características, nomeadamente, baixa pressão de vapor, boa estabilidade térmica etc. Esta nova classe de compostos tem uma vasta gama de aplicações, como por exemplo na área de absorventes para refrigeração.

A aplicação industrial dos líquidos iônicos requer o conhecimento das suas propriedades termofísicas e do comportamento do seu equilíbrio de fases. Este trabalho foca-se, pela primeira vez, no estudo dessas propriedades termodinâmicas de sistemas líquidos iônicos (ILs) + água com a equação de estado soft-SAFT (Statistical Associating Fluid Theory). Os ILs em estudo são: trifluorometanosulfonato de 1-butil-3-metilimidazólio, tiocianato de 1-butil-3-metilimidazólio, trifluoroacetato de 1-butil-3-metilimidazólio, metanosulfonato de 1-butil-3-metilimidazólio, cloreto de 1-butil-3-metilimidazólio, brometo de 1-butil-3-metilimidazólio e tiocianato de 1-butil-3-metilimidazólio.

Neste estudo começou-se por definir esquemas associativos apropriados para cada um dos líquidos iônicos, de seguida com base nos esquemas atribuídos e utilizando dados de densidade à pressão atmosférica otimizaram-se os parâmetros moleculares característicos a cada composto, com o menor erro possível na descrição da densidade.

De seguida passou-se ao estudo do equilíbrio líquido-vapor de sistemas binários compostos por água + líquido iónico, este estudo foi efetuado para sete misturas, compostas pelos ILs anteriormente apresentados e para 3 valores de pressão distintos, nomeadamente: 0.01 MPa, 0.07 MPa e 0.05 MPa. Por fim, passou-se ao estudo dos coeficientes de atividade da água de cada uma das misturas de forma a selecionar o sistema água + IL que melhor satisfaça as exigências da aplicação inicialmente referida.



**keywords**

Ionic liquids, water, liquid-vapour equilibrium, water activity coefficients, soft-SAFT EoS.

**abstract**

The industrial progress is a phenomenon more and more present worldwide, where it is possible to observe an increasing demand for innovation, which therefore results in competitiveness and growth. A consequence of this innovation is the discovery of a novel type of compounds such as: the ionic liquids. These have attracted a high interest in the recent years due to its characteristics, namely: low vapour pressure, good thermal stability, etc. This new class of compounds has a large range of applications, for instance in cooling absorption.

The industrial application of ionic liquids (ILs) requires the knowledge of their thermophysical properties, their phase behaviour and of their mixtures. This work addresses the study of those thermodynamic properties of water + ionic liquids systems using the state equation soft-SAFT EoS, the ILs under study are: 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium tosylate, 1-butyl-3-methylimidazolium trifluoroacetate, 1-butyl-3-ethylimidazolium methanesulfonate, 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium thiocyanate. This work also addresses the description of water activities in ionic liquids.

The study began by starting to define the appropriate association scheme of each ionic liquid, then molecular parameters for each compound were regressed using density data at atmospheric pressure, always trying to find the parameter set with the lowest error in the density description. Then it was initiated the vapour-liquid equilibria study of binary systems composed by water + ionic liquid, this study was made for seven mixtures, composed by the ILs previous mentioned and for three different pressure values, namely : 0.1 MPa, 0.07 MPa and 0.05 MPa. Finally, it was started the water activities coefficients study, of the seven systems in order to select the best pair water + IL that best satisfies the application referred above.



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## Nomenclature

### List of Symbols

$A$	Helmholtz energy
$f$	function
$g_{LJ}$	Radial distribution function of a fluid of a LJ spheres
$k_B$	Boltzman's constant
$k^{HB}$	Association site volume
$k_{mix}^{HB}$	Mixture associating volume
$m$	Number of segments
$M$	Number of association sites
$m_i$	Mass of component i
$N$	Number of points
$p$	Pressure
$Q$	Quadropole
$Q_{exp}$	Experimental quadrupole
$T$	Temperature
$x_i$	Molar fraction of component i
$x_p$	Fraction of the chain with the quadropole
$Z$	Study property
$\varepsilon/k_B$	Dispersive energy between segments forming the chain
$\varepsilon^{HB}/k_B$	Association site energy
$\varepsilon^{HB}/k_B \text{ mix}$	Mixture associating energy
$\mu$	Chemical potential
$\rho$	Molecular density
$\sigma$	Segment size
$\eta$	Binary parameter for correcting deviations in the molecular size
$\xi$	Binary parameter for correcting deviations in the molecular energy
$\gamma$	Water activity coefficient

## List of Abbreviations

%AAD	Percentage average absolute deviation
[C <sub>1</sub> C <sub>1</sub> im][Cl]	1,3-dimethylimidazolium chloride
[C <sub>1</sub> C <sub>1</sub> im][DMP]	1,3-dimethylimidazolium dimethylphosphate
[C <sub>2</sub> mim] [Cl]	1-ethyl-3-methylimidazolium chloride
[C <sub>2</sub> mim][C <sub>2</sub> H <sub>5</sub> SO <sub>4</sub> ]	1-ethyl-3-methylimidazolium ethylsulfate
[C <sub>4</sub> im][BF <sub>4</sub> ]	1,3-dimethylimidazolium tetrafluoroborate
[C <sub>4</sub> mim][Br]	1-butyl-3-methylimidazolium bromide
[C <sub>4</sub> mim] [Cl]	1-butyl-3-methylimidazolium chloride
[C <sub>4</sub> mim][CF <sub>3</sub> CO <sub>2</sub> ]	1-butyl-3-methylimidazolium trifluoroacetate
[C <sub>4</sub> mim][CH <sub>3</sub> SO <sub>3</sub> ]	1-butyl-3-methylimidazolium methanesulfonate
[C <sub>4</sub> mim][CF <sub>3</sub> SO <sub>3</sub> ]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide
[C <sub>4</sub> mim][SCN]	1-butyl-3-methylimidazolium thiocyanate
[C <sub>4</sub> mim] [TOS]	1-butyl-3-methylimidazolium tosylate
[C <sub>6</sub> mim] [Cl]	1-hexyl-3-methylimidazolium chloride
H <sub>2</sub> O	Water
IL	Ionic liquid
ILs	Ionic liquids
LJ	Lennard-Jones
[N <sub>11</sub> (2OH)][Cl]	Choline choride
MPa	Megapascal
[OHC <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate
[OHC <sub>2</sub> C <sub>1</sub> im][Cl]	1-(2-hydroxyethyl)-3-methylimidazolium chloride

## Superscripts

assoc	Association interactions term
chain	Chain term
calc	Calculated value
exp	Experimental value
ideal	Helmholtz energy of an ideal gas at the same temperature and molar density
polar	Polar interactions term
ref	Reference term
total	Total Helmholtz energy

## Subscripts

i	Component i
j	Component j
liq	Liquid phase
vap	Vapour phase

# **1. General Introduction**





## 1. General Introduction

### 1.1 Scope and Objectives

Nowadays the industry has become the economic motor that makes the world to move. All the countries look at the industry to improve their economy, trying to refine and optimize their production. The need for optimizing all the resources implies an accurate knowledge of the behaviour of the raw materials employed, and the study of thermodynamics is a fundamental step to understand all the feasible applications for the compounds and their mixtures.

A group of interesting compounds that have been known for more than a century, and have been attracting major attention within the last two decades, are the ionic liquids<sup>1</sup>. Ionic liquids, also known as liquid electrolytes or ionic melts are a term generally used to refer to salts that form stable liquids. These compounds are receiving great attention in the recent years due to the fact that their properties can be tuned with a well-judged selection of cation-anion pair, giving the opportunity to choose among a vast range of different ionic liquids<sup>2</sup>. These compounds have become a new revolution in both academia and industry, because of their interesting properties and their unique tunable possibilities, which convert them into optimal candidates for many process applications in the chemical industry.

One of the ionic liquids applications is in absorption heat pumps. Previous studies<sup>3</sup> show that absorption heat pumps are important for recovering industry waste heat and it is also important in many fields, such as in the military, air conditioning, steelmaking, chemical industry and in drugs manufacturing. ILs can be used as new cooling absorbents for absorption heat pumps or absorption chillers, where one possible working pair might be composed by water and the IL<sup>3</sup>. Until now, the working pairs are mainly ammonia–water and lithium bromide–water. However, ammonia–water fluids are known to have disadvantages of high working pressure and toxicity, whereas the water–lithium bromide mixture has disadvantages, such as corrosion and crystallization<sup>4</sup>. Thus, it is absolutely necessary to explore new working pairs that can overcome these issues.

In this context, the main objective of this work is to study the possibility of new pairs (water + ILs) that could be used as new cooling absorbents. To achieve this aim it is fundamental the knowledge about the thermodynamic properties and phase equilibrium of water and IL solutions. During this work, several water+ IL systems will be studied. The ILs under study are the ones from the family 1-butyl-3-methylimidazolium<sup>5</sup>, and they are the following : 1-butyl-3-methylimidazolium trifluoromethanesulfonate ( $C_4mim][CF_3SO_3]$ ), 1-butyl-3-methylimidazolium tosylate ( $C_4mim][TOS]$ ), 1-butyl-3-methylimidazolium trifluoroacetate ( $C_4mim][CF_3CO_2]$ ), 1-butyl-3-methylimidazolium bromide ( $C_4mim][Br]$ ), 1-butyl-3-methylimidazolium chloride ( $C_4mim][Cl]$ ), 1-butyl-3-methylimidazolium methanesulfonate ( $C_4mim][CH_3SO_3]$ ) and 1-butyl-3-methylimidazolium thiocyanate

## 1. General Introduction

([C<sub>4</sub>mim][SCN]). These ionic liquids were chosen because there is already experimental VLE data and activity coefficients data available on literature. Once this set of ILs have different anions it is also possible the understanding of the anion effect on the VLE and activity coefficient study.

### 1.2 Refrigeration Systems

The absorption refrigeration technology, which went through more than 100 years, has attracted much attention all over the world, for the reason that it is environmental friendly and could make use of the low-grade energy. Absorption refrigeration uses a source of heat to provide the energy needed to drive the cooling process. This technology requires a working pair, formed by an absorber and a refrigerant. During the process the liquid refrigerant evaporates in a low partial pressure environment, thus extracting heat from its surroundings, and the absorbent absorbs the gaseous refrigerant to reduce its partial pressure in the evaporator and allowing more liquid to evaporate<sup>6</sup>.

The requirements of working fluids of absorption cycles areas are the follows:

- The difference in the boiling point between the pure refrigerant and the mixture at the same pressure should be as large as possible;
- Refrigerant should have high heat of vaporization and high concentration within the absorbent in order to maintain low circulation rate between the generator and the absorber per unit of cooling capacity;
- Transport properties that influence heat and mass transfer, for example, viscosity, thermal conductivity, and diffusion coefficient, should be favourable;
- Both refrigerant and absorbent should be noncorrosive, environmentally, and low cost.

## 1. General Introduction

### 1.3 Ionic Liquids

In the last decade a new class of compounds came into the focus of many research groups around the world: the ionic liquids (IL)<sup>7</sup>. It was in 1998 that Michael Freemantle wrote an article for *Chemical & Engineering News* entitled “Designer Solvents - Ionic Liquids May Boost Clean Technology Development”<sup>8</sup>. There is now an excess of 8000 papers (including over 900 patents or applications) that use the term “ionic liquid”, over 97% of which have been published since Freemantle’s article<sup>9</sup>.

Ionic liquids, also known as liquid electrolytes, ionic melts, ionic fluids or liquid salts is a term generally used to refer to salts that form stable liquids<sup>10</sup>, they are composed of large organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature (by definition ILs are liquid at temperatures below 373 K). ILs are promising chemicals or solvents for green chemical processes because of their unique physicochemical properties. The most important property that differentiates ILs from other common solvents currently used is that they have negligible vapour pressure<sup>11</sup>, ILs can be considered as practically nonvolatile, thus, at even harsh conditions they do not emit vapours and are not released into the atmosphere via evaporation. Their second remarkable property is their enormous liquid range (as wide as approximately 300–350°C) in comparison with other common solvents<sup>12</sup>. Another important property that ILs possess is their unique solvent power, ILs are excellent solvents for a wide range of organic and inorganic materials<sup>13</sup>, this great potential of ILs to dissolve many simple organic or inorganic compounds and very complex chemicals, is mostly caused by their extraordinary affinity to act as hydrogen-bond donors and/or acceptor, and the degree of charge delocalization on their anions<sup>1</sup>. In addition to other properties, it is important to highlight the lipophilicity of ILs. In general, lipophilicity of ILs increases with the length of the alkyl chain substituent on both cations and anions<sup>1</sup>.

Other important property of ILs is related with the ions coordination, the ILs are usually composed of poorly coordinating ions, so they can provide a highly polar noncoordinating environment<sup>14</sup>. This unique feature is strongly beneficial for reactions in ILs due to the fact that polar solvents usually coordinate to the metal center of catalysts blocking the active site, whereas non polar non coordinating solvents do not dissolve the catalyst, this property can also be seen as an ionic liquid application. This class of compounds is also characterized by a good thermal stability and high ionic conductivity<sup>15</sup>.

In summary, the ILs present a spectrum of physical and chemical properties much different than the traditional organic or inorganic solvents. Just as their solubility, the physical properties of ILs can also be tuned by modifying an anion or a cation as well as by

## 1. General Introduction

simple change in, for example, the chain length of the alkyl substituent in the cation or anion. This combination of cations and anions allows the synthesis of more than  $10^6$  different ILs. Despite this large value, until now only a small number (on the order of  $10^3$ ) of these compounds are described and characterized in literature<sup>16</sup>.

The exceptional properties of these compounds cause a huge demand for them. Their excellent thermal and chemical stabilities and good tunable solubility, combined with their catalytic properties opened way for a variety of applications for ILs. They were originally developed by electrochemists for use in low-temperature applications, IL electrolytes have found applications in battery systems, solar cells<sup>17</sup> and electrochemical capacitors<sup>18</sup>. However, in the last 30 years, the principal use of ILs has been dedicated to chemical reactions. In these processes ILs are mainly used as more sustainable solvents and in replacing volatile organic solvents. Another great scientific area, in which ILs are broadly used and studied, is in the processes of separation and purification. ILs are able to selectively extract a specific compound out of a gas or liquid mixture<sup>19</sup>.

Other applications of ILs include their use as cleaning solvents, lubricants, heat-transfer fluids and storage media, for which they are suitable because of their solubility behaviour<sup>19</sup>, high thermal stability, large liquid temperature range and wetting behaviour. One of the applications of the ILs being investigated is the absorption refrigeration<sup>3</sup>. A brief presentation of the ILs applications is present on figure 1.

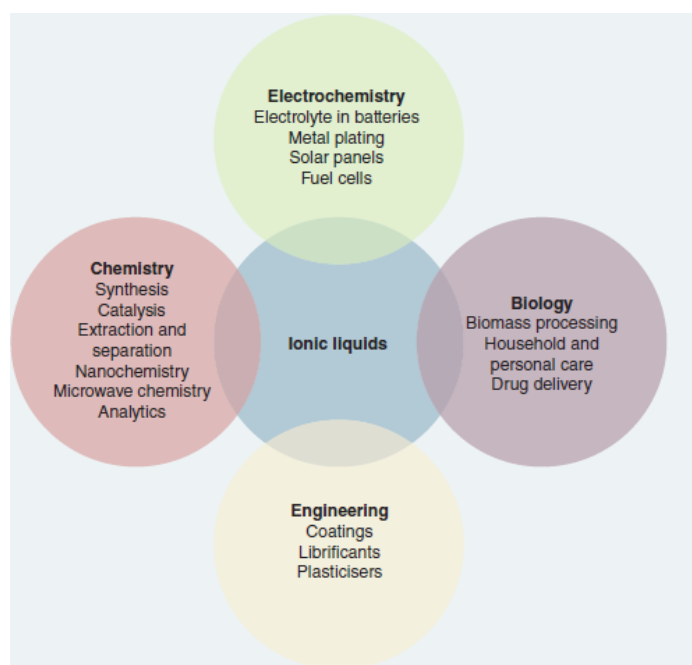


Figure 1 - Large-scale application of ILs<sup>1</sup>

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Due to the large amount of possible ionic liquids, they were organized by families, thus facilitating their classification. The types of ionic liquid available have also been extended to include new families and generations of ionic liquids with more specific and targeted properties, some of these families are described on figure 2.

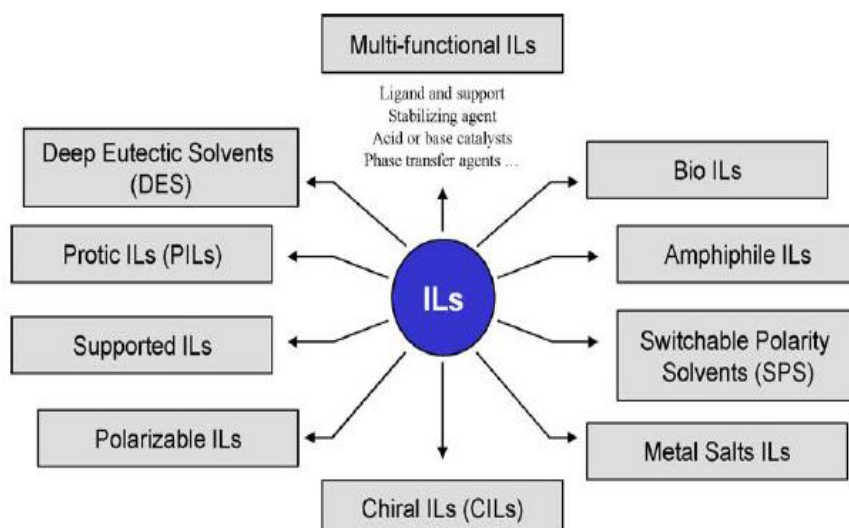


Figure 2 - Evolution of IL generations.

In spite of the variety of ILs, many have already been prepared. The most studied ILs are based on the ammonium, phosphonium, pyridium or imidazolium cations, and on the tetrafluoroborate  $[\text{BF}_4]^-$ , hexafluorophosphate  $[\text{PF}_6]^-$ , trifluoromethylsulfonate  $[\text{CF}_3\text{SO}_3]^-$  or bis(trifluoromethylsulfonyl)imide  $[\text{NTf}_2]^-$  anions<sup>20</sup>. Some illustrative cations and anions are represented in Figure 3.

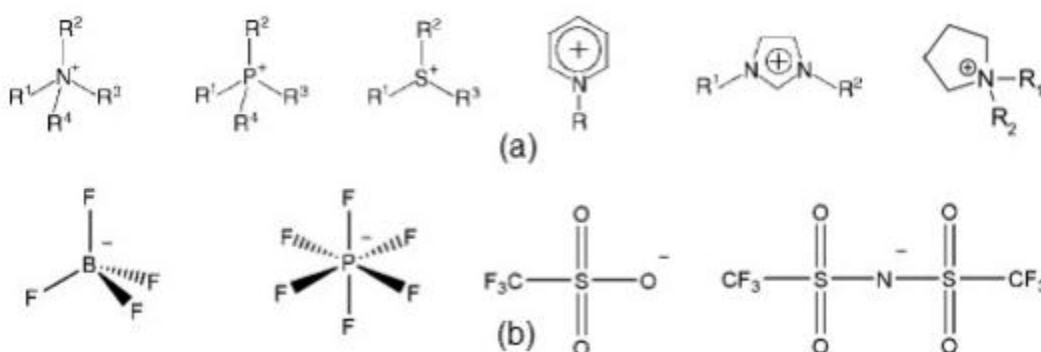


Figure 3 - Structure of common cations a) and anions of ionic liquids b).

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Knowing how the structure of ILs influences their physical and chemical properties is very important. Thus, it is relevant to quantify fundamental properties such as density, viscosity, surface tension, heat capacity, thermal and electrochemical stability and solubility that allow the assessment of suitability from ILs to specific applications, as well as to design new ILs<sup>21</sup>. Understanding the origins of the properties of ILs and finding a way to control them by design would provide a wide array of challenges and opportunities to the physical chemistry community<sup>22</sup>.

### 1.4 ILs + Water Systems

Absorption chillers or absorption heat pumps are important energy-saving devices which can be driven by a lot of low-grade thermal energy, such as solar energy and industrial waste heat from industrial process, so these devices can play an important role in improving energy utilization efficiency and reducing environmental pollution and carbon dioxide emissions<sup>23</sup>. The performance of absorption cycles depends on the thermodynamic properties of the working pairs consisted of a refrigerant and an absorbent. Up to now, the commonly-used working pairs are ammonia and water solutions ( $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) and aqueous solution of lithium bromide ( $\text{H}_2\text{O}$  and  $\text{LiBr}$ )<sup>23</sup>. However, the corrosion, crystallization and toxicity are their inevitable weakness in industrial applications. Therefore, seeking for more advantageous working pairs with good thermal stability, no corrosion and crystallization, has become a research focus in the recent years. Because of the excellent properties of ILs, it is possible that these compounds can be used as new types of absorbent or coolants for absorption chillers or absorption heat pumps.

With the goal to find profitable new working pairs, numerous literature works have been published: Zuo et al.<sup>5</sup> suggested the system water + 1-ethyl-3-methylimidazolium ethylsulfate ( $[\text{C}_2\text{mim}][\text{C}_2\text{H}_5\text{SO}_4]$ ) as a new working pair, during this work, the properties, vapour pressure, heat capacity and density were measured, and it was used the NRTL model to calculate the vapour pressure. The heat capacity and density were correlated with the simple polynomial functions of temperature and molar fraction; Wang et al.<sup>24</sup> proposed the application of the system constituted by water + 1,3-dimethylimidazolium chloride ( $[\text{C}_1\text{C}_1\text{im}][\text{Cl}]$ ) where the vapour pressure of the two systems were measured using the boiling point method. Wang et al concluded that the water + 1,3-dimethylimidazolium chloride ( $[\text{C}_1\text{C}_1\text{im}][\text{Cl}]$ ) pair is a promising alternative working set for improving the performances of the absorption cooling cycle; Zhang et al.<sup>25</sup>

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simulated a single effect absorption cycle using the water + 1,3-dimethylimidazolium dimethylphosphate ( $[\text{C}_1\text{C}_1\text{im}][\text{DMP}]$ ) and compared the results with those of aqueous solution of lithium bromide ( $\text{H}_2\text{O}+\text{LiBr}$ ) already tested. Zhang et al concluded that this new working pair has a similar cycle performance as that of  $\text{H}_2\text{O} + \text{LiBr}$ ; Kim et al.<sup>26</sup> showed broad theoretical work on various mixtures of refrigerants and ILs as working pairs for the absorption refrigeration system, concluded that the solubility of the refrigerants in the ILs and their temperature dependence affected the circulation ratio. Was also verified that cations with shorter alkyl chains are preferred due to more sensitive dependence of the solubility on temperature ; Wu et al.<sup>27</sup> measured vapour pressures and the VLE of water and 1,3-dimethylimidazolium tetrafluoroborate ( $[\text{C}_4\text{mim}][\text{BF}_4]$ ) mixtures and suggested them as promising working pairs on a comparison basis with ( $[\text{C}_1\text{C}_1\text{im}][\text{Cl}]$ )<sup>27</sup> and 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{mim}][\text{BF}_4]$ )<sup>28</sup>; Kim et al.<sup>28</sup> measured the vapour pressures of water + 1-butyl-3-methylimidazolium bromide ( $[\text{C}_4\text{mim}][\text{Br}]$ ), water + ( $[\text{C}_4\text{mim}][\text{BF}_4]$ ) and water + 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ( $[\text{OHC}_2\text{C}_1\text{im}][\text{BF}_4]$ ) systems in broad concentration and temperature ranges, for that the boiling-point method was used; Nie et al.<sup>29</sup> suggested water + 1-(2-hydroxyethyl)-3-methylimidazolium chloride ( $[\text{OHC}_2\text{C}_1\text{im}][\text{Cl}]$ ) as a novel alternative working pair for the absorption heat pump cycle. Thermodynamic properties of the system including vapour pressure, density, and heat capacity were measured. The vapour pressures of the binary system were determined by the boiling-point method, the densities and heat capacities were correlated by the polynomial equations on temperature and concentration.

Recently Carvalho et al.<sup>30</sup> measured the VLE of 1-ethyl-3-methylimidazolium chloride ( $[\text{C}_2\text{mim}][\text{Cl}]$ ), 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}][\text{Cl}]$ ), 1-hexyl-3-methylimidazolium chloride ( $[\text{C}_6\text{mim}][\text{Cl}]$ ), and choline chloride ( $[\text{N}_{11(2\text{OH})}][\text{Cl}]$ ) with water and ethanol using a new isobaric microbulliometer at pressures ranging from 0.05 to 0.1 MPa, some of the working pairs could be appropriate for absorption chillers or absorption heat pumps, since they have negative deviations from Raoult's Law. Thus, knowledge about thermodynamic properties and phase equilibria of water + IL solutions is fundamental to determine their applicability as absorption refrigeration systems. The previous studies can be supported by thermodynamic models.

Thermodynamic models are an important tool used in chemical industry. They are seen as an advantage, since they save time when comparing with experimental measurements. Sometimes due to the extremely temperature and pressure conditions only the use of thermodynamic models is possible and safe.

Several thermodynamic models have been applied to describe thermodynamic properties and phase equilibria of IL aqueous solutions: Wang et al.<sup>31</sup> applied the Square-Well Chain Fluid with Variable Ranges EoS (SWCF-VR) to describe the VLE of several systems constituted by water +  $[\text{Tf}_2\text{N}]$ -based ILs. The imidazolium-based IL were modelled as a diblock square-well chain, one block is the substituent alkyl group and the other

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block is the imidazolium ring-anion. The model parameters of the imidazolium-anion are obtained by fitting the experimental pressure-volume-temperature (pVT) data. Banarjee et al.<sup>32</sup> applied the Conductor-like Screening Model for Realistic Solvation (COSMO-RS), a predictive model based on unimolecular quantum chemistry calculations, to predict the VLE of water + alkylimidazolium based ILs. The predictions were very good for a large number of systems containing a variety of functional groups. The model is also able to predict the low- and high-boiling azeotrope formation. Freire et al.<sup>33,34</sup> studied the VLE and the LLE of a large range of water + IL mixtures using COSMO-RS. The VLE predictions showed to be more accurate in respect to the available experimental data, describing well all the ILs structural modifications in their phase behaviour. Nevertheless, for the LLE predictions some model limitations were found, especially for the anions influence. Carvalho et al.<sup>30</sup> applied the NRTL model to correlate VLE data of binary mixtures of water + IL and ethanol + IL and the non-ideal behaviour of the ionic liquid phase solutions. In that work a new microbullimeter for the measurement of the boiling temperatures of ionic liquid systems was developed and validated with success. A good fit of the experimental VLE data was obtained, which makes the NRTL model suitable to support the preliminary design of extractive distillation schemes. Vega et al.<sup>22</sup> used soft-SAFT to describe the LLE of water + imidazolium based ILs, using three maximum association sites mimicking the strong interactions between the anion and cation.

### 1.5 soft-SAFT EoS

Understanding the thermodynamic properties of pure substances and their mixtures is essential for the design of processes used in the chemical industry, unfortunately, such data are often not available and in some cases are difficult to measure experimentally. An alternative for this issue is the use of simulation methods and equations of state (EoS)<sup>35</sup>. One of the most EoS successfully used at the moment is the Statistical Associating Fluid Theory (SAFT).

The SAFT EoS was originally developed by Chapman et al.<sup>36</sup>, using the first order thermodynamic perturbation theory (TPT1) due to Wertheim<sup>37, 38, 39, 40</sup>. There are several versions of the SAFT equation available in literature<sup>41</sup>. A review on the development, applications, and different versions of SAFT-type equations was supplied by Muller and Gubbins<sup>42</sup>.

The success of the equation on its different versions is confirmed by the number of published works since its development.



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The explanation for the success of SAFT-based equations is its solid statistical mechanics basis, which allows a physical interpretation of the system. It provides a framework in which the effects of molecular shape and interactions on the thermodynamic properties can be separated and quantified.

In its various shapes SAFT has been widely used to correlate and predict experimental results of a wide variety of pure substances and their mixtures<sup>43</sup>. The EoS is written in terms of the Helmholtz free energy ( $A^{res}$ )<sup>44</sup>, defined as the difference between the total Helmholtz energy ( $A^{total}$ ) and that of an ideal gas at the same temperature and molar density ( $A^{ideal}$ )<sup>45</sup>.

The residual Helmholtz energy can be then calculated as the sum of each independent contribution. The general expression of the SAFT equation is given by:

$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} + A^{polar} \quad Eq. 1$$

where the terms *ref*, *chain*, *assoc* and *polar* are respectively connected to the reference term, the formation of the chain, the associating and the polar terms. Each term is related with a specific characteristic, like,  $A^{ref}$  accounts for the pairwise intermolecular interactions of the reference system,  $A^{chain}$  evaluates the free energy due to the formation of chains from units of the reference system,  $A^{assoc}$  takes in to account the contribution due to site-site association and  $A^{polar}$  accounts for electrostatic contributions.

The principal difference between all types of SAFT EoS is in the reference term, that can be a hard-sphere fluid with a dispersion term, a Lennard-Jones fluid, a hard-chain fluid, or a square-well fluid<sup>46</sup>. In this work, the SAFT type equation used is the soft-SAFT, that is also described by equation 1. For this specific EoS the reference term is a Lennard Jones spherical fluid (LJ), which accounts for the repulsive and attractive interactions of the monomers that formed the chain<sup>47</sup>. soft-SAFT EoS has been applied to several ionic liquid systems<sup>15</sup>. Imidazolium based ionic liquids with the bis(trifluorosulfonyl)imide anion  $[Tf_2N]^-$  are one of the most successfully ILs already investigated using this equation of state.

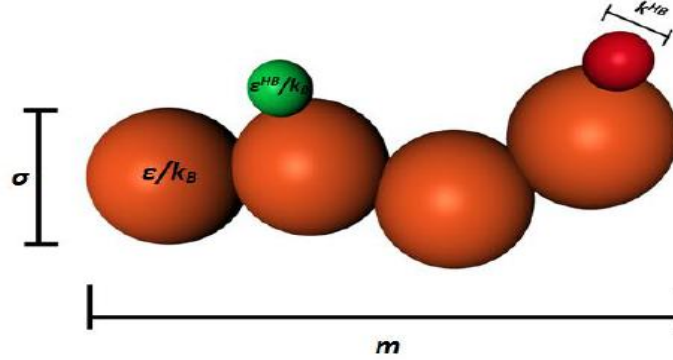
Recently other ionic liquids have been studied using the soft-SAFT EoS. Pereira et al.<sup>48</sup> measured the  $CO_2$ ,  $N_2O$ ,  $CH_4$  and  $N_2$  solubility in  $[C_2mim][CH_3OHPO_2]$ . This IL was modelled as an LJ chain with two associating sites, one site A, representing the interaction of the anion oxygen with the cation, and one site B, representing the anion delocalized charge, due to the second anion oxygen atom.

In order to apply the soft-SAFT equation, a molecular model for each compound integrating the mixture needs to be proposed and the best molecular parameters values must be established. The number of parameters depends on the compound being a non-associating or an associating compound. In the first case, compounds are characterized by

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three molecular parameters: the number of segments ( $m$ ), the segment size ( $\sigma$ ) and the dispersive energy between segments ( $\varepsilon/k_B$ ). If there is association two more parameters are necessary: the energy ( $\varepsilon^{HB}/k_B$ ) and volume ( $k^{HB}$ ) of associating per site. These set of values are obtained by fitting experimental density data and vapour pressure.

A hypothetical model of an associating molecule modelled by soft-SAFT is presented in figure 4.



**Figure 4 - Molecular modelled by the soft-SAFT equation.**

As previously discussed, the reference term is different in each type of SAFT EoS, this term usually describes the properties of the individual units that compose the chain. In this work, it's used the LJ equation. There are two accurate LJ equations of state that are temperature and density functions: the Benedict-Webb-Rubin EoS from Jhonson et al<sup>49</sup> and the perturbed virial expansion with a reference hard sphere term from Kolafa and Nezbeda et al<sup>50</sup>. The equation used in this work is the one projected by Jhonson et al, and consists of a modified Benedict-Webb-Rubin EoS to which simulation data was fitted and the equation parameters determined, the equation can also be used in mixtures through the use of the Van der Waals one-fluid theory<sup>16</sup>.

When applied to mixtures, the corresponding expressions for the parameters involved in the reference fluid are:

$$m = \sum_{i=1}^n x_i m_i \quad \text{Eq. 2}$$

$$\sigma = \frac{\sum_{i=1}^n \sum_{j=1}^n m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^n \sum_{i=1}^n m_j m_i x_j x_i} \quad \text{Eq. 3}$$

$$\frac{\varepsilon}{k_B} \times \sigma^3 = \frac{\sum_{i=1}^n \sum_{i=1}^n m_i m_j x_i x_j \varepsilon_{ij} \sigma_{ij}^3}{\sum_{i=1}^n \sum_{i=1}^n m_i m_j x_i x_j} \quad \text{Eq. 4}$$

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The indices  $i$  and  $j$  are related with the species in the mixture, the crossed interaction parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}$  presented in the previous equations are calculated using the generalized Lorentz-Berthelot combining rules:

$$\sigma_{ij} = \eta_{ij} \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad \text{Eq. 5}$$

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad \text{Eq. 6}$$

where  $\eta_{ij}$  and  $\xi_{ij}$  are the binary adjustable parameters for the species  $i$  and  $j$ , these two parameters have the role to correct some deviations in molecular size and energy of the compounds that form the mixture.

The reference term is expressed as a function of the chain molar fractions, the chain and associating terms come from Wertheim's theory and are usually similar in all type of SAFT equations.  $A^{chain}$  is obtained as a function of the chain length of the different species,  $m_i$ , and the pair correlation function of the reference fluid mixtures, and it is represent by the equation 7:

$$A^{chain} = \rho k_B T \sum_i x_i (1 - m_i) \ln g_{JL} \quad \text{Eq. 7}$$

where  $\rho$  is the molecular density,  $k_B$  is the Boltzmann's constant,  $T$  is the temperature,  $x_i$  is the molar fraction of component  $i$ ,  $m$  is the chain length and  $g_{JL}$  is the radial distribution function of a LJ mixture of spheres at contact length,  $\sigma$ .

The associating term,  $A^{assoc}$ , is expressed as the sum of contributions of all associating sites of component  $i$ :

$$A^{assoc} = \rho k_B T \sum_i x_i \left( \sum_\alpha \ln X_i^\alpha - X_i^\alpha + \frac{M_i}{2} \right) \quad \text{Eq. 8}$$

where  $M_i$  is the number of association sites in component  $i$  and  $X_i^\alpha$  is the mole fraction of molecules of component  $i$  nonbonded at site  $\alpha$ .

The last term presented in the general expression of SAFT equation (Eq. 1), the  $A^{polar}$ , is used for the study of linear symmetrical molecules, like carbon dioxide, nitrogen, aromatic compounds or acetylene<sup>15</sup>. This term is calculated introducing two new parameters, the quadrupole moment,  $Q$ , and the  $x_p$  that represents the fraction of segments that contains the quadrupole. These additional parameters era related by the next equation:

$$Q = Q_{exp} \cdot x_p \quad \text{Eq. 9}$$

where  $Q_{exp}$  is the experimental quadrupole.

In order to use the soft-SAFT equation for a precise system a molecular model for each compound has to be chosen. This part of the work must be done in the better way, because the choice of the model will influence the quality of the molecular parameters

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calculated later. Thus molecular parameters of pure compound are calculated by fitting experimental data for vapour pressure and saturated liquid density over a wide range of temperatures using the next expressions<sup>51</sup>:

$$f_1 = (m, \sigma, \varepsilon/K_B, \varepsilon^{HB}/k_B, k^{HB}) = \sum_{i=1}^N \{\rho_i^{exp} - \rho_i^{calc}(p_i^{exp}, T_i^{exp})\}^2 \quad Eq. 10$$

$$f_2 = (m, \sigma, \varepsilon/K_B, \varepsilon^{HB}/k_B, k^{HB}) = \sum_{j=1}^N \{\mu_{i,liq}^{calc}(p_i^{exp}, T_i^{exp}) - \mu_{i,vap}^{calc}(p_i^{exp}, T_i^{exp})\}^2 \quad Eq. 11$$

where  $N$  is the number of experimental points used in the fitting,  $i$  is the label for every experiment used,  $T_i^{exp}$ ,  $\rho_i^{exp}$  and  $p_i^{exp}$  are the temperature, the liquid density and the vapour pressure, respectively, corresponding to the experimental point  $i$ ,  $\rho_i^{calc}$  is the saturated liquid density predicted by the EoS at the temperature  $T_i^{exp}$ ,  $\mu_{i,liq}^{calc}$  and  $\mu_{i,vap}^{calc}$  are the chemical potentials of the liquid and vapour side respectively, predicted by the equation at the temperature  $T_i^{exp}$  and pressure  $p_i^{exp}$ . The function  $f_1$  represents the difference between the experimental and predicted saturated liquid density and the function  $f_2$  is the difference between the liquid and vapour predicted chemical potentials. The iterative process over when  $f_1$  or  $f_2$  are less than  $10^{-6}$ .

Once defined the compounds to study it is necessary the knowledge of a tool that allows the study of the thermodynamic properties. With the goal to achieve the description of pure compounds and mixtures physical properties many equations of state were developed. The soft-soft EoS, proposed by Vega and co-workers based on the original Statistical Associating Fluid Theory (SAFT) is one of the most successful associating EoS, and will be applied to the previous systems for the first time during this work.

In order to propose the best working pair (water + IL) the vapour-liquid equilibrium and the activity coefficients of each system will be studied. The ionic liquids presented before were studied for the first time during this thesis, using the soft-SAFT EoS, therefore association schemes and molecular parameters had to be identified and proposed to each IL. Experimental data always report the reality, showing what happens at certain conditions, while modelling saves money and can be used to determine a set of experiments. This shows that experimental work and the modelling part are equally necessary for a precise description of a fluid or a mixture<sup>52</sup>.

## **2. soft-SAFT EoS Molecular Models**



## 2. soft-SAFT EoS Molecular Models

Modelling the phase equilibrium and thermodynamic properties of systems in which molecules exhibit associating interactions remains a challenging problem in the chemical industry. The selection of a model able to represent the characteristics of the compound to be described is a key element for accurate predictions from any molecular-based EoS. Soft-SAFT depends on the pre-adjustments of molecular parameters for each compound, these parameters are obtained by fitting experimental density data and vapour pressure. For ionic liquids, due to their negligible vapour pressure only density data at atmospheric pressure are considered in the regression. All the pure compounds are represented through the molecular parameters:  $m$  the chain length,  $\sigma$  the size segment,  $\varepsilon/k_B$  the dispersive energy between segments,  $\varepsilon^{HB}/k_B$  the associating energy per site and  $k^{HB}$  the volume of associating per site.

In order to evaluate the precision of the results, the description of the pure data is evaluated by the percentage average absolute deviation, defined as the difference between experimental data and the results given by soft-SAFT EoS, as described by equation 12:

$$\%AAD Z = \left| \frac{1}{N} \sum_{i=2}^N \frac{Z^{exp} - Z^{calc}}{Z^{exp}} \right| \times 100 \text{ Eq. 12}$$

The development of a molecular model for the pure compounds is a fundamental step before any calculation can be done with soft-SAFT, the basis of Wertheim's perturbation theory is the fact that it considers the possibility of association between the molecules. A molecule can have one or more associating sites, the theory allows an infinite number of sites, although in practise, more than four seems quite unrealistic for a molecule. An associating site is characterized by a noncentral potential placed near the perimeter of a molecule.

Previous studies already exist, where associating sites and molecular parameters were proposed. Various compounds have been considered and molecular parameters were already studied and applied to, like alkanes in water<sup>45</sup> and polymers<sup>53</sup>. Of relevance for this work, as described below, two ionic liquids and water were previously considered.

Just in a recent period, soft-SAFT has been extended to ILs and their mixtures by Vega and co-workers<sup>54</sup>, and one of the families of ILs under study was the  $[C_n\text{-mim}][\text{Tf}_2\text{N}]$ <sup>55</sup>. Presented in figure 5 is a proposed associating scheme for  $[C_4\text{mim}][\text{Tf}_2\text{N}]$ <sup>15</sup>.

## 2. soft-SAFT EoS Molecular Models

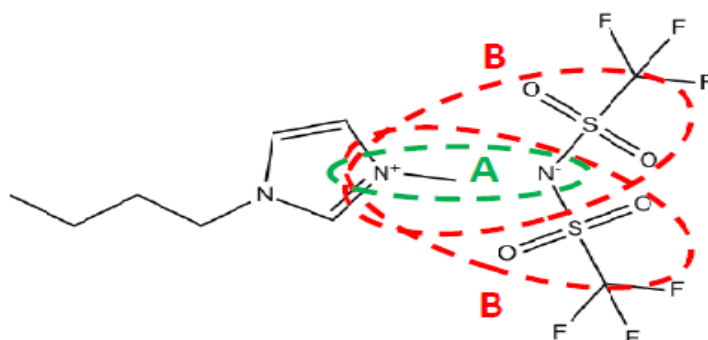


Figure 5 - Proposed associating scheme for [C<sub>4</sub>mim][Tf<sub>2</sub>N] by Andreu et al.<sup>15</sup>

All the compounds [C<sub>n</sub>mim][Tf<sub>2</sub>N], with n between 2-8, were modelled as a LJ chains with three associating sites in each molecule. According to these interactions, it is used an “A” site representing the nitrogen atom interactions with the cation and two “B” sites representing the delocalized charge due the oxygen molecules on the anion, each type of associating site is identically defined , but only AB interactions between different ILs are allowed<sup>15</sup>.

Another compound that has already studied in the 1-butyl-3-methylimidazolium thiocyanate ionic liquid ([C<sub>4</sub>mim][SCN]), since this ionic liquid is part of the water + IL systems that are present in this work and its molecular model has already been defined in a previous work, by Pereira et al.<sup>16</sup> , a molecular scheme was proposed by Pereira et al.<sup>16</sup> considering one associating site as depicted in figure 6.

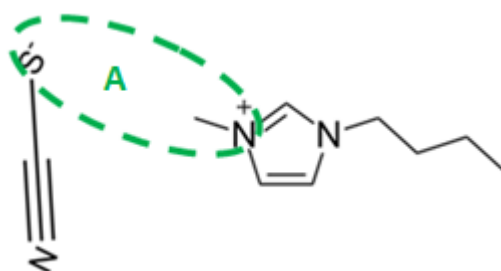


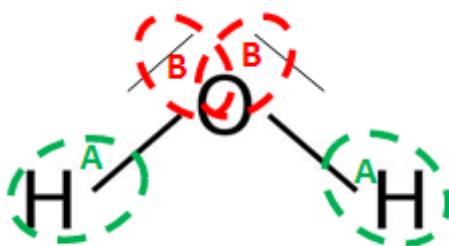
Figure 6 - Proposed associating scheme for [C<sub>4</sub>mim][SCN] by Pereira et al.<sup>16</sup>



## 2. soft-SAFT EoS Molecular Models

The IL was modelled as a LJ chain with one associating site, "A", where the "A" site represent the specifics interactions due to the IL charge and asymmetry.

Finally is presented another compound that has been intensively studied, the water, this molecule will be considered in this work in the VLE studies and lately during the analysis of the water activities coefficients of water + ionic liquids systems. Several empirical models have been developed along the years<sup>56</sup> for this compound. Different site models have been considered for water within different SAFT type approaches, and a comparison between the performance of the models considering two, three and four associating sites was done by Clark et al.<sup>57</sup>. This study verified that the four-site model performs better than the other two. Therefore in this work it was decided to use the four-site model. A representative scheme is presented in figure 7, where it is show the two sites, "A", representing the two hydrogen atoms in the water molecule and the other two sites, "B", representing the lone pairs of electrons of the oxygen. Only AB interactions are allowed, no AA or BB interactions are permitted.



**Figure 7 - Proposed scheme for water by Clark et al.<sup>57</sup>**

Once selected the associating schemes for  $[H_2O]$  and  $[C_4mim][SCN]$ , the molecular parameters,  $m, \sigma, \epsilon/k_B, \epsilon^{HB}/k_B$  and  $k^{HB}$  were determined by fitting the experimental density data at atmospheric pressure in the case of  $[C_4mim][Tf_2N]$  and  $[C_4mim][SCN]$ . In the case of water the adjusted molecular parameters were fitted using density and vapour pressure values. These values were already determined in previous studies and the same values will be used in this work. The values are listed on Table 1 which will be presented later in this chapter together with the new molecular parameters achieved for the ILs studied for the first time in this thesis.

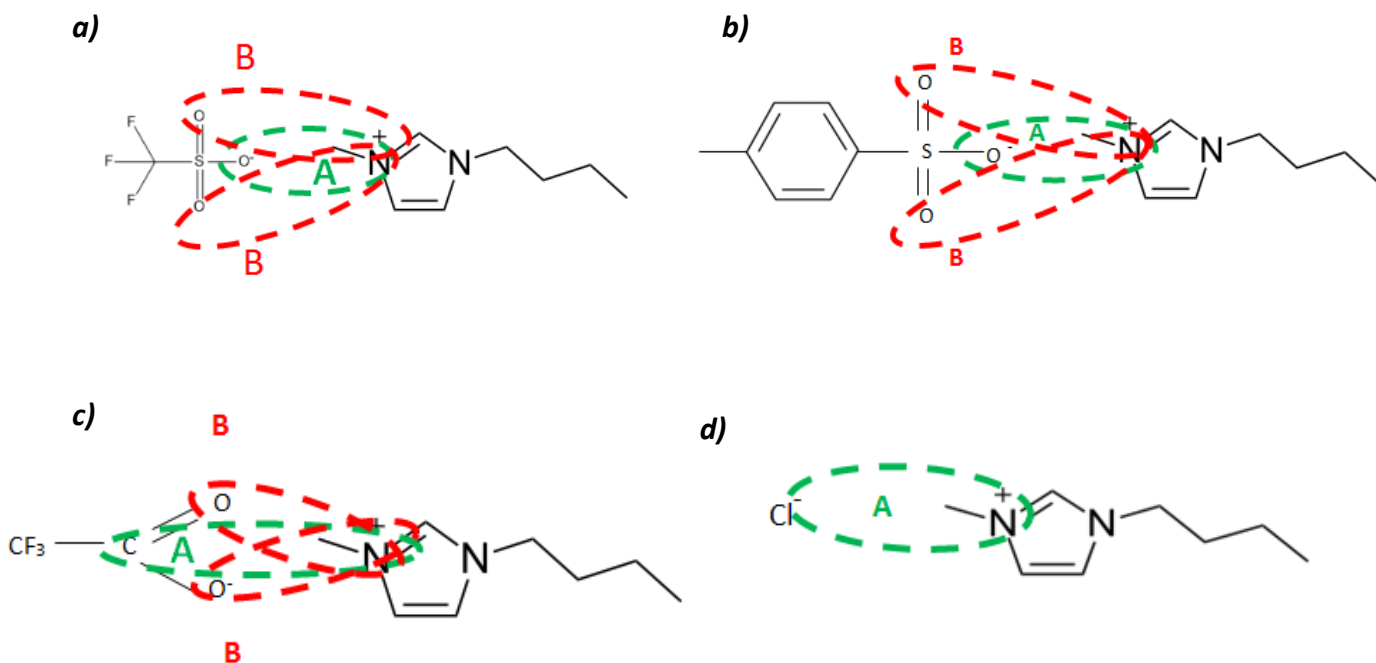
## 2. soft-SAFT EoS Molecular Models

### 2.1 New ILs studied with soft-SAFT

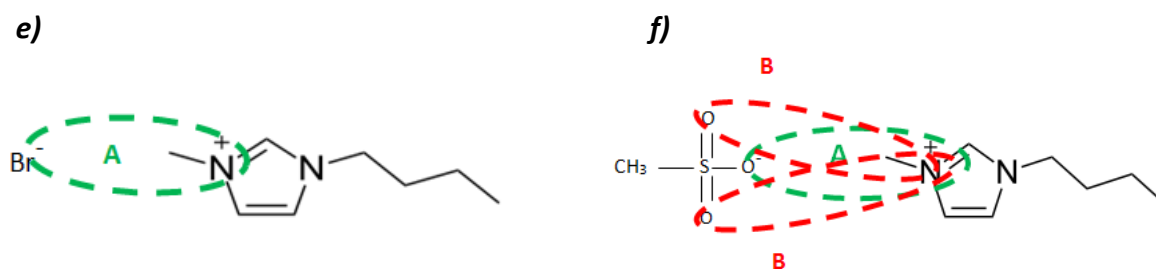
As mentioned before, during this work, for the first time the VLE of mixtures composed by water and ILs will be analyzed, specifically: 1-butyl-3-methylimidazolium trifluoromethanesulfonate ( $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ ), 1-butyl-3-methylimidazolium thiocyanate ( $[\text{C}_4\text{mim}][\text{SCN}]$ ), 1-butyl-3-methylimidazolium tosylate ( $[\text{C}_4\text{mim}][\text{TOS}]$ ), 1-butyl-3-methylimidazolium trifluoroacetate ( $[\text{C}_4\text{mim}][\text{CF}_3\text{CO}_2]$ ), 1-butyl-3-methylimidazolium bromide ( $[\text{C}_4\text{mim}][\text{Br}]$ ), 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}][\text{Cl}]$ ) and 1-butyl-3-methylimidazolium methanesulfonate ( $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$ ).

Therefore, it is indispensable the knowledge of the molecular parameters of those compounds, on the other hand there are no molecular parameters already adjusted in literature for the set of ILs presented above. Hence, they will be adjusted for the first time in this study.

Following the above mentioned approach, it is required to select the association scheme of each ionic liquid. They were modelled as LJ chains with one and three associating sites as it is illustrated in figure 8.



## 2. soft-SAFT EoS Molecular Models



**Figure 8 - Schemes of association adopted in this work for the ILS [C<sub>4</sub>mim][CF<sub>3</sub>SO<sub>3</sub>] (a), [C<sub>4</sub>mim][TOS] (b), [C<sub>4</sub>mim][CF<sub>3</sub>CO<sub>2</sub>] (c), [C<sub>4</sub>mim][Cl] (d), [C<sub>4</sub>mim][Br] (e) and [C<sub>4</sub>mim][CH<sub>3</sub>SO<sub>3</sub>] (f).**

In the case of one associating site, such as for [C<sub>4</sub>mim][Cl] and [C<sub>4</sub>mim][Br] presented in figures 8-**d**) and 8-**e**) respectively, the ionic liquids were modelled as a LJ chain with one associating site, "A", where the "A" site represents the specific interactions due to the IL charges and asymmetry. In the case of the ILs modelled with three associating sites representing the cation-anion interactions, one "A" type association site represents the strong interactions due to the anion's oxygen (figure 8-**a**), **c**), **f**) with the cation and two "B" sites represent the delocalized charge due to the other oxygen molecules on the anion, allowing only AB interactions between different ionic liquid molecules. Finally the IL presented on figure 8-**b**) also was modelled considering three associating sites, one "A" type site represent the interactions due to the cation nitrogen and two "B" sites represent the oxygen molecules.

The selection of the number of associating sites was based on previous works where similar schemes were proposed for compounds of the same ILs cation family, imidazolium ionic liquids<sup>22</sup>.

Other tool that is able to select the number of associating sites is the COSMO-RS<sup>58</sup>, a quantum chemical-based thermodynamic prediction model, where calculations can be used to generate surface charge density representations and  $\sigma$ -profile  $p(\sigma)$  graphs, which gives the relative amount of surface with polarity on the surface of a molecule. An approximate pattern between the number of peaks and associating points to be considered can be evaluated. However, it is important to remark that COSMO-RS is not used in this work. This set of ionic liquids was previously studied by Passos et al.<sup>3</sup> using a different SAFT type, the PC-SAFT, during this work ILs were treated as molecular associating species with two associating sites (2B association scheme) per IL.

Once established the association scheme the molecular parameters are determined by fitting them against experimental density data. The adjusted molecular parameters are listed in Table 1. Molecular parameters for [H<sub>2</sub>O] were taken from the literature<sup>22</sup>.

## 2. soft-SAFT EoS Molecular Models

**Table 1 - Ionic liquids molecular parameters and density results.**

	$m(adm)$	$\sigma(\text{Å})$	$\varepsilon/k_B (K)$	$\varepsilon^{HB}/k_B (K)$	$k^{HB}(\text{Å}^3)$	%AAD
[H <sub>2</sub> O] <sup>22</sup>	1.000	3.154	365.0	2388	2932	---
[C <sub>4</sub> mim][SCN]	4.966	3.878	420.0	3850	2850	0.10
[C <sub>4</sub> mim][CF <sub>3</sub> SO <sub>3</sub> ]	5.466	3.986	371.5	3700	6939	0.084
[C <sub>4</sub> mim][TOS]	4.891	4.385	380.6	3580	5515	0.076
[C <sub>4</sub> mim][CF <sub>3</sub> CO <sub>2</sub> ]	4.179	4.256	360.7	3700	2477	0.014
[C <sub>4</sub> mim][CH <sub>3</sub> SO <sub>3</sub> ]	4.156	4.218	374.2	3700	4615	0.090
[C <sub>4</sub> mim][Cl]	4.647	3.819	487.3	3342	2518	0.016
[C <sub>4</sub> mim][Br]	6.650	3.426	438.1	3700	2368	0.096
[C <sub>4</sub> mim][CF <sub>3</sub> SO <sub>3</sub> ] <sub>(2)</sub>	3.494	4.579	318.2	3700	6639	0.23
[C <sub>4</sub> mim][Cl] <sub>(2)</sub>	5.393	3.537	332.3	3525	8000	0.36
[C <sub>4</sub> mim][Br] <sub>(2)</sub>	5.201	3.639	330.7	3700	5219	0.64

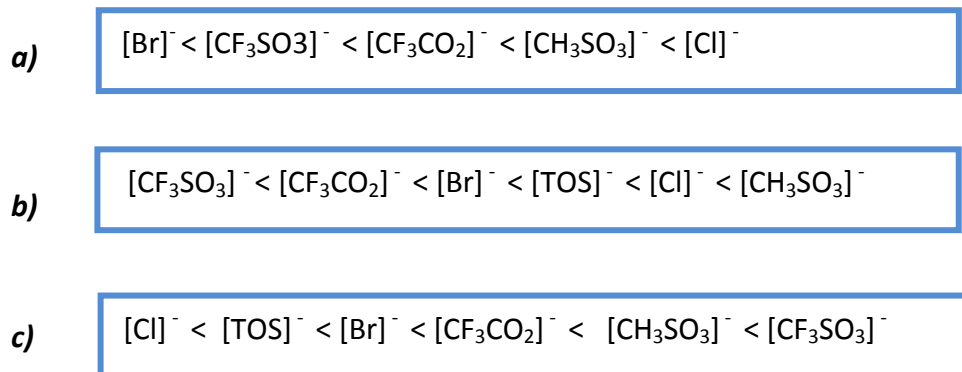
As can be seen by the presented %AAD values these sets of parameters seem to allow a good description of the experimental density. The values for the chain length  $m$ , the segments, diameter,  $\sigma$ , and the dispersive energy between segments,  $\varepsilon/k_B$ , for all the compounds are in the same range as the values previously obtained for the [C<sub>4</sub>mim]<sup>+</sup> ionic liquids with the [Tf<sub>2</sub>N]<sup>-22</sup>, [BF<sub>4</sub>]<sup>-22</sup> and [Pf<sub>6</sub>]<sup>-22</sup> anions. In table 1 it is also presented another set of parameters identified by the subscript 2. It will be explained later the need for a second parameter's optimization for the [C<sub>4</sub>mim][CF<sub>3</sub>SO<sub>3</sub>], [C<sub>4</sub>mim][Cl] and [C<sub>4</sub>mim][Br] ionic liquids.

One of the most important aspects of ILs when envisaging their use for replacing typical molecular solvents relies on the specific interactions occurring between the solvent and the dissolved solute. To evaluate this effect, recent studies<sup>59</sup> have been done and some of them show a relation between the polarity of the ILs and the molecular parameters for each ionic liquid. Recently, Claudio et al.<sup>59</sup> proposed an extended scale of the ability on the ionic liquid anion to hydrogen-bond, through hydrogen-bonding interaction energies, occurring in equimolar cation-anion mixtures, calculated with COSMOS-RS. In figure 9-a) it is presented the scale proposed by Claudio et al to the new ILs under study in this work. This figure represents the increase of the hydrogen-bonding interaction energy. As higher the value of the energy is the more polar is the anion, and, consequently, higher are the expected associating parameters values.

Other scale related to the ions polarity is the scale proposed by Khan et al.<sup>60</sup>, they analyzed the interactions between the ionic liquids and water through the activity

## 2. soft-SAFT EoS Molecular Models

coefficients. The proposed scale it is presented on figure 9-**b)** .Figure 9-**c)** represents the hydrogen-bonding interaction energies, reached during the molecular parameters optimization for all the new ILs identified.



**Figure 9 - a) Hydrogen-bonding interaction energies scale proposed by Claudio el al.<sup>59</sup> , b) Intensity of interactions of the inions with water through activity coefficients proposed by Khan et al.<sup>60</sup> and c) scale identified during the molecular parameters fitting and**

Analyzing figures 9-**a)** and 9-**b)** and comparing with figure 9- **c)** it is visible that the scale proposed during this work isn't in agreement with the scales previously proposed. Therefore it was tried to find new parameters that were in line with the scale presented in figure 9-**c)**, since figure 9-**a)** hasn't information about the  $[\text{TOS}]^-$  anion. The values achieve are in Appendix A. However the new parameters obtained have considerably high *AAD* % values, so it was decided that the final values for the molecular parameters are the first set showed in table 1.

After being determinated the molecular parameters for each IL, the density values produced by the molecular parameters were computed. In figures 10 to 15 are illustrated the temperature-density diagrams for all the ILs considered in this work for the first time with the soft-SAFT.

## 2. soft-SAFT EoS Molecular Models

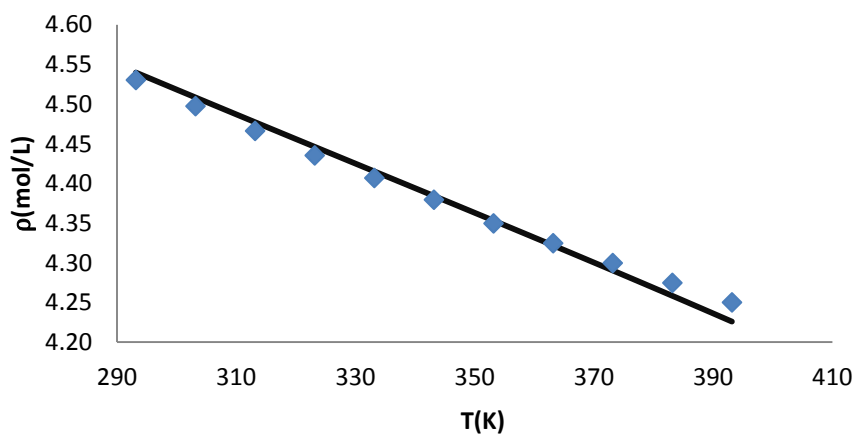


Figure 10 - Temperature – Density diagram for [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

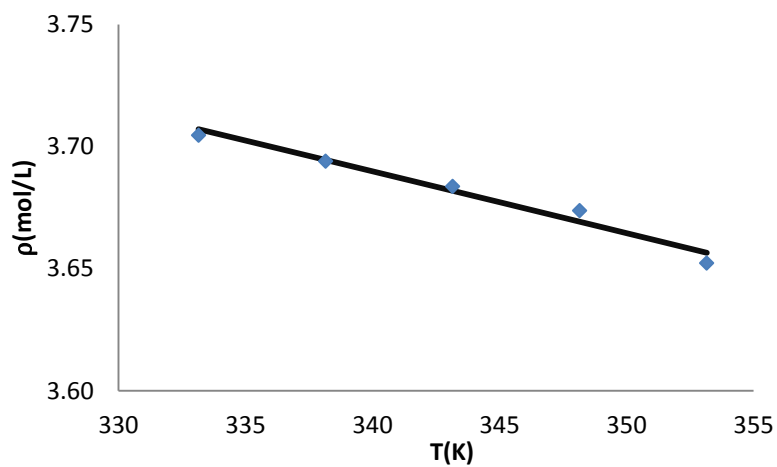


Figure 11 - Temperature – Density diagram for [C<sub>4</sub>mim] [TOS]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

## 2. soft-SAFT EoS Molecular Models

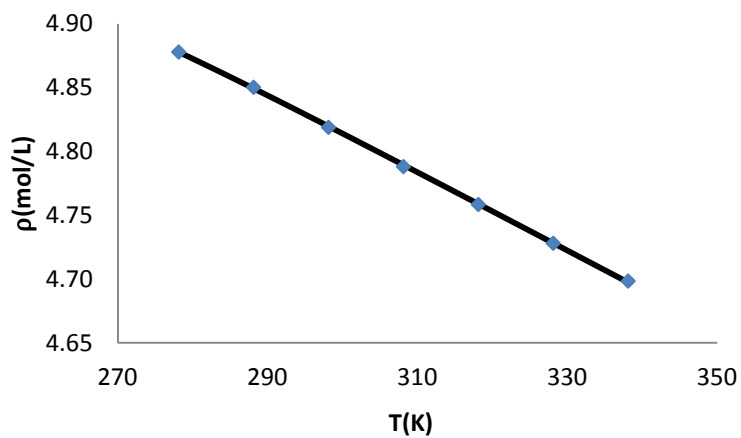


Figure 12 - Temperature – Density diagram for [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

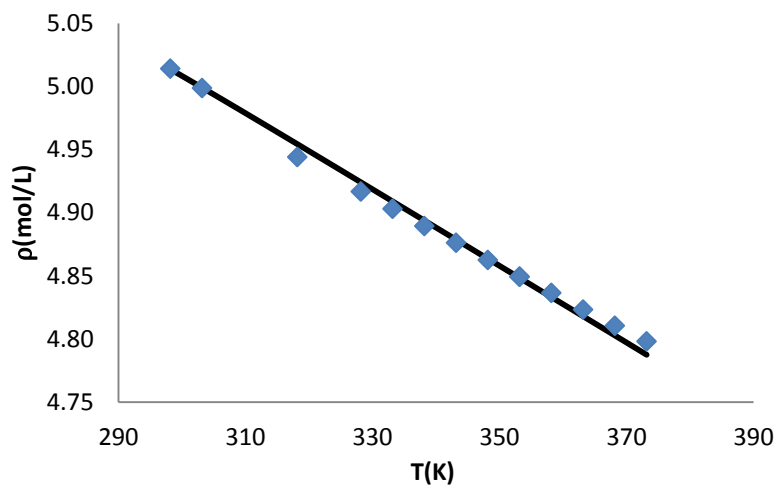


Figure 13 - Temperature – Density diagram for [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

## 2. soft-SAFT EoS Molecular Models

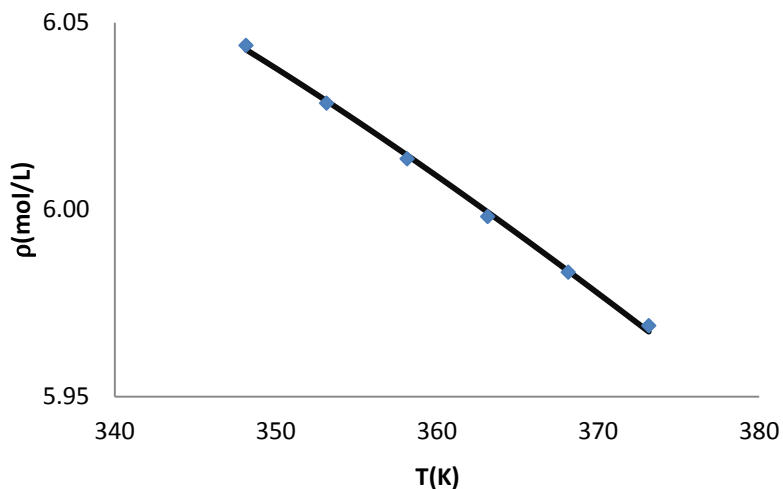


Figure 14 - Temperature – Density diagram for [C<sub>4</sub>mim] [Cl]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

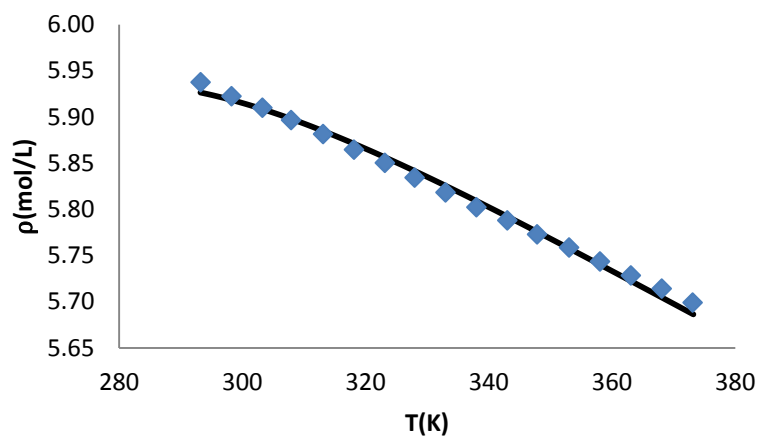


Figure 15 - Temperature –Density diagram for [C<sub>4</sub>mim] [Br]. Solid lines represent soft-SAFT EoS results and the points represent the experimental values<sup>3</sup>.

All the figures show a good agreement between the soft-SAFT EoS results and the experimental values taken from the literature. Deviations between the soft-SAFT results and the experimental data are identified on table 1, and are below 0.7 %.



### **3. Description with the soft-SAFT EoS of the VLE of water + IL systems**



### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

Accurate thermodynamic properties of pure compounds and mixtures, in particular phase equilibria, are needed over a wide range of temperatures and pressures for the optimization of existing and the design of new process and/or materials in chemical industry, accordingly the industrial application of ionic liquids requires the knowledge of their physical properties and phase behaviour.

#### 3.1 VLE study

Once the molecular parameters of each compound were established, it is then feasible to describe the phase equilibria of the binary systems. In this section it will be investigated and presented the applicability of the soft-SAFT EoS to describe the vapour-liquid equilibrium of the mixtures composed by the ionic liquids considered above and water. Recalling, these are: 1-butyl-3-methylimidazolium trifluoromethanesulfonate ( $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$ ), 1-butyl-3-methylimidazolium tosylate ( $[\text{C}_4\text{mim}][\text{TOS}]$ ), 1-butyl-3-methylimidazolium trifluoroacetate ( $[\text{C}_4\text{mim}][\text{CF}_3\text{CO}_2]$ ), 1-butyl-3-methylimidazolium bromide ( $[\text{C}_4\text{mim}][\text{Br}]$ ), 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}][\text{Cl}]$ ), 1-butyl-3-methylimidazolium methanesulfonate ( $[\text{C}_4\text{mim}][\text{CH}_3\text{SO}_3]$ ) and 1-butyl-3-methylimidazolium thiocyanate ( $[\text{C}_4\text{mim}][\text{SCN}]$ ).

In addition to the pure compound molecular parameters it is also necessary the knowledge of the mixture cross-associating volume,  $k^{HB}$ , and the mixture cross-associating energy,  $\varepsilon^{HB}/k_B$ . These parameters are usually calculated using common mixing rules. However they show not to be appropriate to deal with water systems<sup>61</sup> and needed to be regressed from experimental data. Accordingly, both parameters were optimized to the VLE data of each water+ IL system during the VLE study. The VLE calculations were done considering three different pressures: 0.1 MPa, 0.07 MPa and 0.05 MPa. After the selection of the set  $k^{HB}$  and  $\varepsilon^{HB}/k_B$  other two parameters are adjusted, which are the binary adjustable parameters,  $\eta_{ij}$  and  $\xi_{ij}$ . These parameters are used to correct possible deviations in molecular size and energy of the segments forming the two compounds in the mixture.

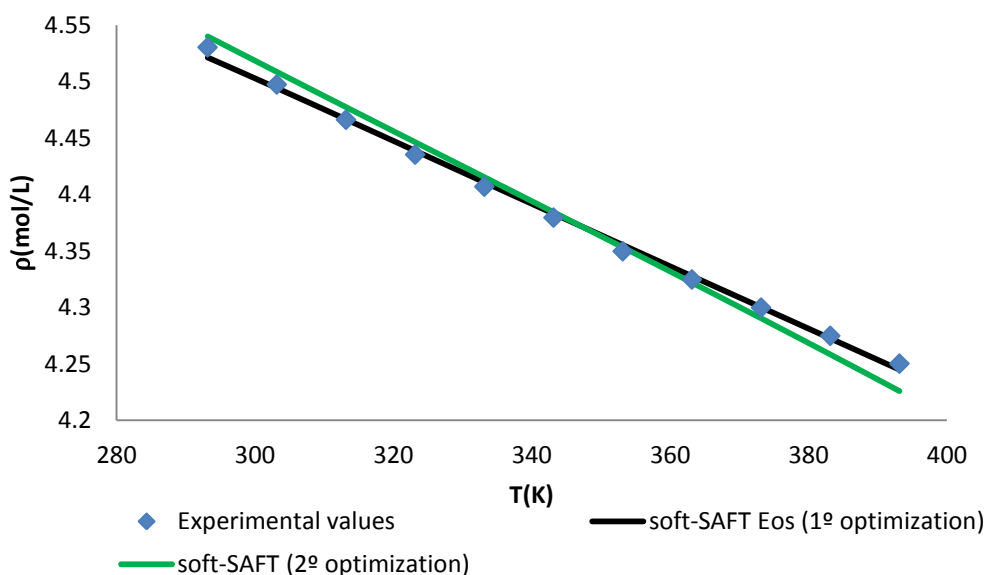
##### 3.1.1 H<sub>2</sub>O+ $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$

The H<sub>2</sub>O+  $[\text{C}_4\text{mim}][\text{CF}_3\text{SO}_3]$  system was modelled taking into account four and three associating sites, respectively. In a first attempt to produce results similar to the experimental VLE data, already analysed and published<sup>3</sup> it was used the set of molecular parameters presented in table 1 (soft-SAFT EoS Molecular Models chapter).

Unfortunately, that set of values didn't produce consisting results for the VLE, and therefore it was decided to try a new set of parameters, so it was done a second

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

molecular parameters optimization, also presented in table 1 with the subscript 2. Presented in figure 16 is the density-temperature diagram for the [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>], taking into account the two sets of data calculated from soft-SAFT and experimental values.



**Figure 16 – Density – temperature diagram for [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>].**

Through figure 16 it is perceptible that the second optimization has a higher percentage average absolute deviation ( $\%AAD = 0.23$ ) than the first optimization ( $\%AAD = 0.084$ ), due to the poorer description of the density temperature dependency. Despite this fact, the ionic liquid molecular parameters used to describe the vapour-liquid equilibrium were the values fitted in the second regression. As mentioned before, two new parameters are also necessary to be regressed from experimental data to describe the mixture VLE: the cross-associating volume,  $k^{HB}$ , and the cross-associating energy,  $\varepsilon^{HB}/k_B$ . The selection of these two parameters was based on a comparison between the values given by the model and the experimental data, using the size and the energy parameters equal to one.

The  $k^{HB}$  and  $\varepsilon^{HB}/k_B$  values used in this system were: 2585 ( $\text{\AA}^3$ ) and 3292 (K), respectively. After the cross-association values were chosen the size and the energy binary parameters values were also regressed to describe the VLE. The best results were achieved when:  $\eta_{ij} = 1.0$  and  $\xi_{ij} = 1.1$ . It was only necessary to use one binary parameter different from one, the energy parameter, and even the required value is quite close to unity. In addition, the same  $\xi_{ij}$  was used for all the three pressures considered.

The vapour-liquid equilibria results for the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>] are present on figure 17.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

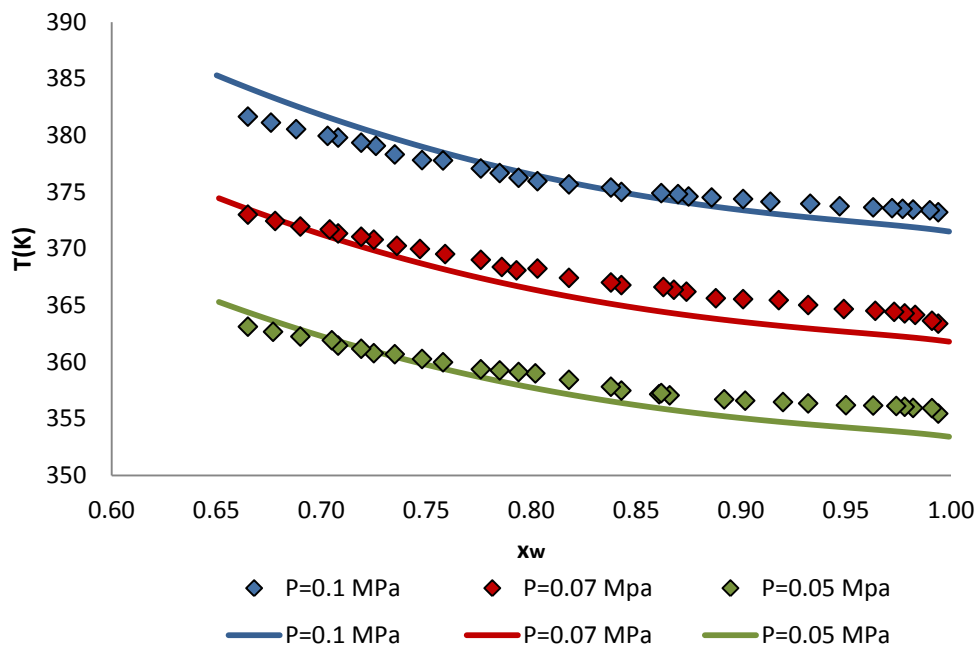


Figure 17 – Temperature - water fractions diagram for the system  $H_2O + [C_4mim][CF_3SO_3]$  at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>

Based on figure 17 it's visible that the results produced by soft-SAFT are in agreement with the experimental values measured by Passos et al.<sup>3</sup>. The *AAD* % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.29%, 0.41 % and 0.35 % respectively, in temperature. Taking into account those values it is concluded that the soft-SAFT EoS is a capable model to describe the vapour-liquid equilibria of the system composed by water + 1-butyl-3-methylimidazolium trifluoromethanesulfonate.

#### 3.1.2 $H_2O + [C_4mim][CF_3CO_2]$

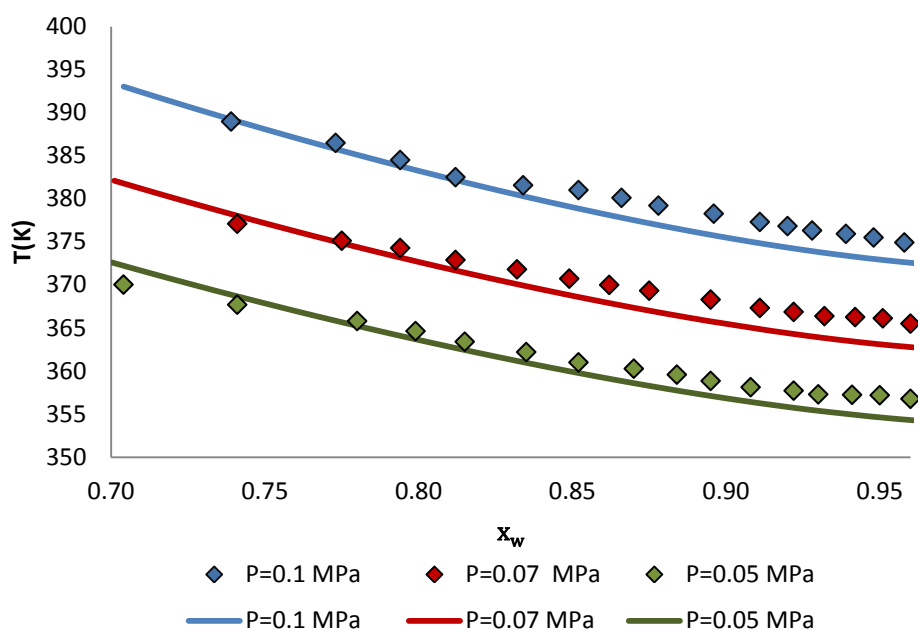
The system composed of  $H_2O + [C_4mim][CF_3CO_2]$  was modelled considering four association sites for water and three for the ionic liquid. The vapour-liquid equilibrium of this mixture was analysed considering the molecular parameters presented in table 1, and in this case it wasn't necessary a second optimization.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

Again, the cross-association energy and volume parameters were regressed from the experimental VLE data, using size and energy binary parameters equal to one. The set of values for  $k^{HB}$  and  $\varepsilon^{HB}/k_B$  that yield VLE data in good comparison with the experimental data were: 3510 ( $\text{\AA}^3$ ) and 3111 (K). Comparing these values with the values used in the previous system ( $k^{HB} = 3292$  ( $\text{\AA}^3$ ), ;  $\varepsilon^{HB}/k_B = 2585$  (K) ) it is noticed that the volume value is higher in this case, although the energy value is smaller than the one of the previous systems.

After the parameters  $k^{HB}$  and  $\varepsilon^{HB}/k_B$  have been established, the results were improved by using binary parameters different from the unity and the correspondent effects on VLE data were analysed. Hence, the pair  $\eta_{ij}$  and  $\xi_{ij}$  that produced the best VLE results are, 1 and 1.17, respectively. A slight change was necessary to produce viable VLE data, contrary to the previous system where the  $\xi_{ij}$  value was equal to 1.1. In the both systems it was verified that changing the  $\eta_{ij}$  value doesn't affect the VLE data given by soft-SAFT and the set of binary parameters was also kept constant to all the pressures considered. The vapour-liquid equilibria obtained for the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{CF}_3\text{CO}_2]$  system are depicted on figure 18.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems



**Figure 18 – Temperature - water fraction diagram for the system  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{CF}_3\text{CO}_2]$  at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

Observing figure 18 it is noticed that the soft-SAFT results correctly describe the experimental data reported by Passos et al.<sup>3</sup> The *AAD* % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.55%, 0.57 % and 0.47 % respectively, in temperature. The *AAD* % values are similar to the ones presented for previous system for which the soft-SAFT EoS also computed excellent VLE results.

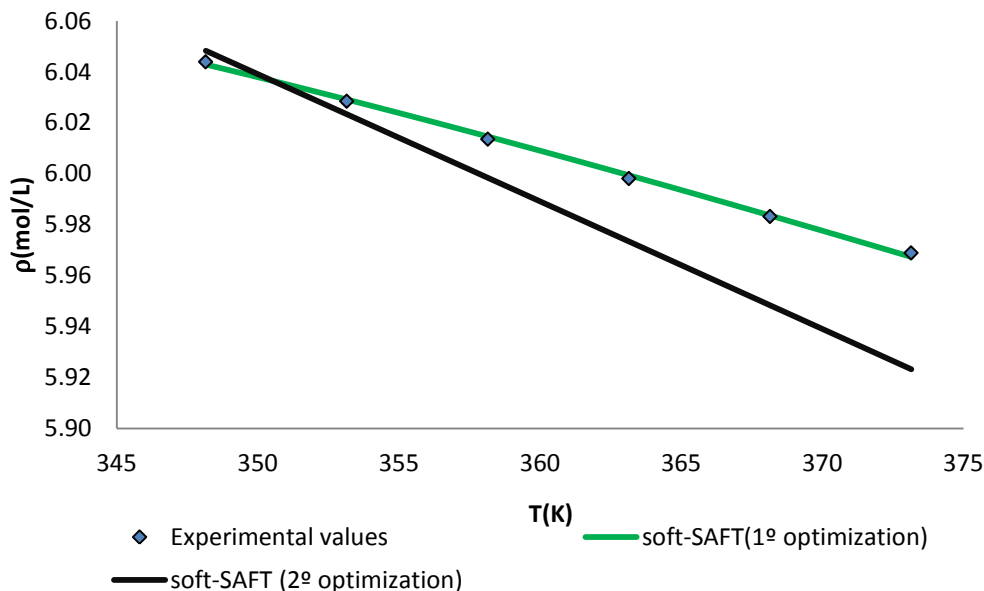
#### 3.1.3 $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{Cl}]$

The  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{Cl}]$  system was modelled taking into account four and one associating sites for each pure compound, respectively. In the first effort to produce results similar to the VLE experimental data already published it was used the set of molecular parameters presented in table 1.

Despite the lower error on density,  $\%AAD = 0.016$ , of the molecular parameters optimized, the VLE data produced using that set of values are in disagreement with the experimental data. Therefore, it was decided once again to try to use a new set of molecular parameters, so it was performed a second molecular parameters optimization, which results are also presented in table 1 with the subscript 2.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

Presented in figure 19 is the density-temperature diagram, considering the two sets of values computed from soft-SAFT and the set of experimental values.



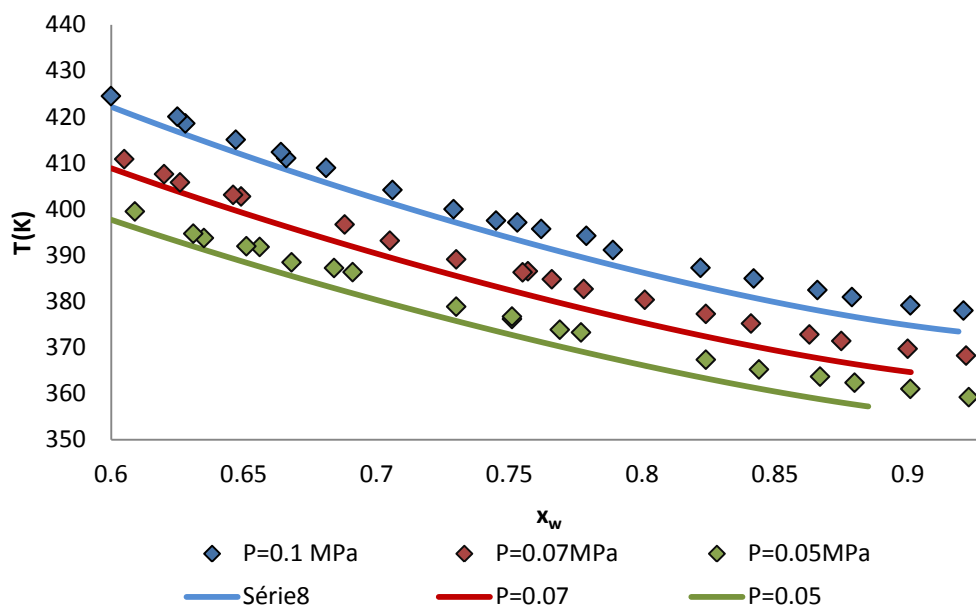
**Figure 19 – Density - temperature diagram for [C<sub>4</sub>mim] [Cl].**

The second optimization has an error of,  $\%AAD = 0.362$ , much higher than the error present in the first optimization, as well as a quite poor description of the density temperature dependency. In spite of this higher value, the obtained VLE data using the second optimization are consistent with the experimental values. The optimized values used for the cross-association energy and cross-associating volume of the mixture were 3432 (K) and 3820 ( $\text{\AA}^3$ ), respectively. The  $\varepsilon^{HB}/k_B$  value used in this case is in the same range than the value used in the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{SO}_3]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{CO}_2]$  systems. These values can be used in future studies of similar systems.

The VLE calculations were initially done considering the binary adjustable parameters,  $\eta_{ij}$  and  $\xi_{ij}$  equal to one. To improve the results, during the calculations other values were also adjusted and the best results were achieved when:  $\eta_{ij} = 1.18$  and  $\xi_{ij} = 1.27$ . In this case, it was observed that for achieving good results it was necessary to change both, the size and the energy parameters. On the contrary to what happened with the previous systems the binary parameters values are more different than the reference values of one. Nevertheless, and as before, these parameters were kept constant for all the pressures considered. The vapour-liquid equilibrium obtained for the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Cl}]$  system is illustrated in figure 20.



### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems



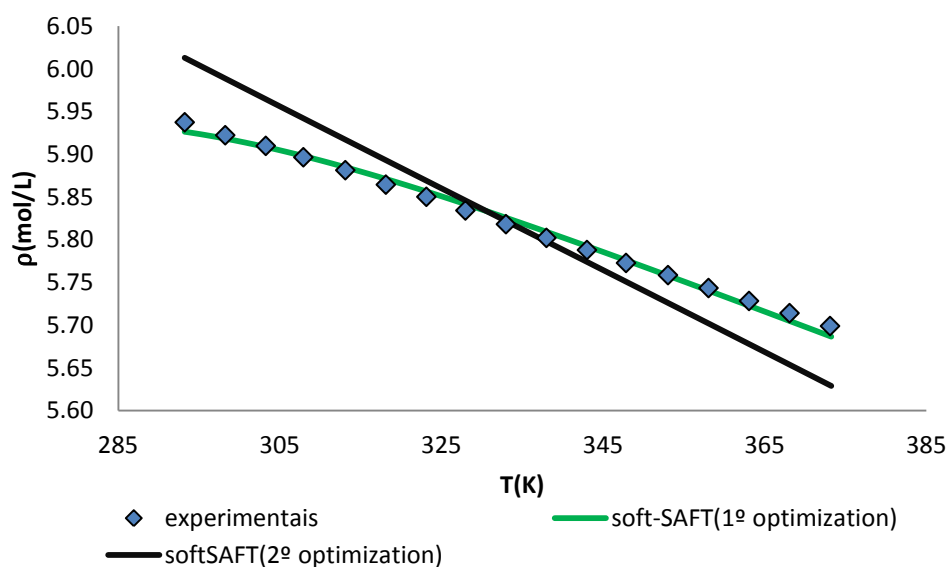
**Figure 20 - Temperature - water fraction diagram for the system  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{Cl}]$  at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

Based on figure 20 it's perceptible that soft-SAFT is able to calculate the vapour-liquid equilibrium of a mixture composed by water and 1-ethyl-3-methylimidazolium chloride. The experimental values used in this thesis were proposed by Passos et al<sup>3</sup>. The *AAD* % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.96%, 1.2 % and 2.4 % respectively, in temperature.

#### 3.1.4 $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{Br}]$

Considering now the vapour-liquid equilibrium study for the binary mixture  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{Br}]$ , it was applied an associating scheme with four associating sites to water and was proposed one associating site for the pure compound, 1-ethyl-3-methylimidazolium bromide. The use of the molecular parameters obtained by fitting experimental density data at atmospheric pressure didn't produce viable VLE data, therefore a second parameters optimization was again necessary. Presented in figure 21 is the density-temperature diagram representing the two set of values obtained with the molecular parameters optimized as well as the experimental data.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems



**Figure 21 – Density - temperature diagram for [C<sub>4</sub>mim] [Br].**

The %AAD associated to each set was of 0.096 for the first optimization and 0.642 of for the second optimization.

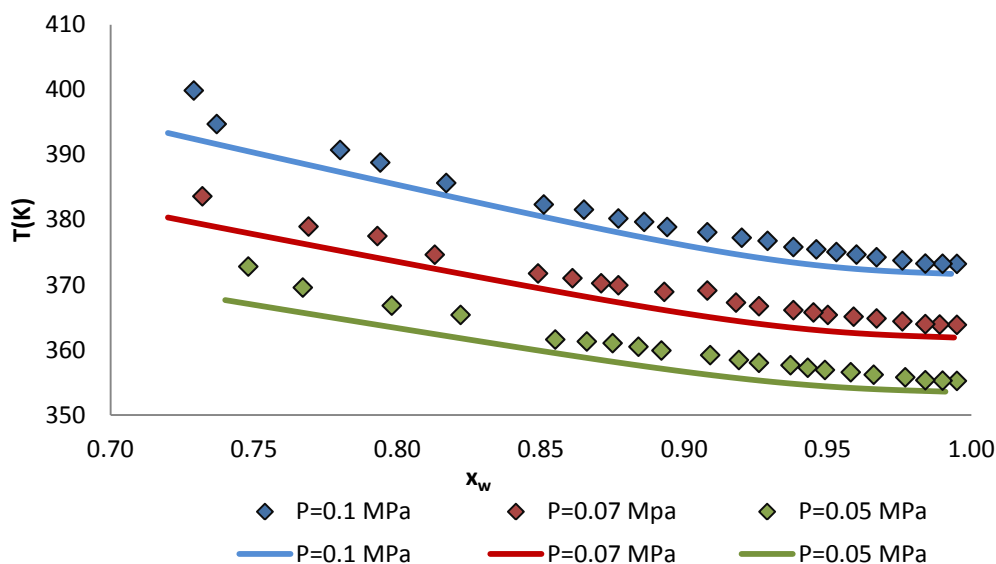
It was also seen a deterioration of the density description with the temperature with the second set of parameters. However, the molecular parameters obtained in the second optimization produced viable VLE results. Using binary parameters equal to one, the optimized values used for the cross-association energy and cross-associating volume of the mixture were 3432 (K) and 3180 (Å<sup>3</sup>), respectively. On the contrary to what was initially intended, it wasn't possible to find a common set of adjustable binary parameters that produced acceptable VLE results for the three different pressures analysed. Therefore, it was necessary to use different binary parameters values for each pressure. Nevertheless, it was still possible to use the size parameter equal to one for all the pressures considered. The final values are presented in table 2.

**Table 2 - Binary parameters consider for the pressures: 0.1 MPa, 0.07 MPa and 0.05 MPa.**

P(MPa)	$\eta_{ij}$	$\xi_{ij}$
0.1	1	1.26
0.07	1	1.24
0.05	1	1.22

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

The values for  $\xi_{ij}$  used in this system are relatively different from unit, as happened with the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl], and it is visible that high pressure values require higher binary parameters. The vapour-liquid equilibria obtained for the H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br] system are illustrated in figure 22.



**Figure 22 – Temperature - water fraction diagram for the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br] at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

As it is presented in figure 22 the soft-SAFT equation seems to be a good tool to describe the VLE data of the mixture composed by water and 1-butyl-3-ethylimidazolium bromide, with values in line with the experimental values produced by Passos et al.<sup>3</sup> The AAD % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.68%, 0.75 % and 0.77 % respectively, in temperature.

#### 3.1.5 H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS]

Analysing now the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS], it was modelled considering four association sites for water and three for the ionic liquid. Once established the association scheme and the molecular parameters for both pure compounds (Molecular Parameters chapter) it is now possible the VLE study. The  $k^{HB}$  and  $\varepsilon^{HB}/k_B$  values that produce the best VLE results were: and 2750 (Å<sup>3</sup>) and 2810 (K)

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

,respectively. Following the approach used in the previous system, the VLE calculations were initially done considering the binary parameters,  $\eta_{ij}$  and  $\xi_{ij}$ , equal to one and during the calculations another values were used trying to find the best set to improve the modelling results. Presented on table 3 are the final values selected.

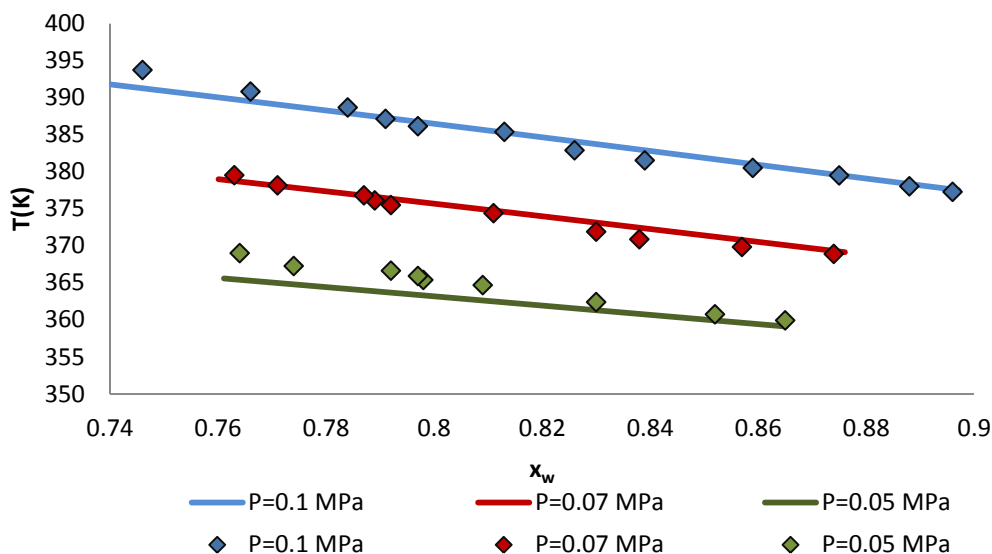
**Table 3 - Binary parameters considered for the pressures: 0.1 MPa, 0.07 MPa and 0.05 MPa.**

P(MPa)	$\eta_{ij}$	$\xi_{ij}$
0.1	1	1.26
0.07	1	1.26
0.05	1	1.22

Similarly to what happened with the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br], it wasn't also possible to use a single pair of binary parameters for all the pressures under analysis. The  $\xi_{ij}$  values that produced better results are again significantly different from unit for the 3 pressures. Only the parameter  $\xi_{ij}$  was modified, because it was observed that changing the  $\eta_{ij}$  value didn't affect the VLE results, so it was decided to consider  $\eta_{ij}$  equal to one and just make changes in the  $\xi_{ij}$  value. Also here it is noticed that the  $\xi_{ij}$  value is similar to the values used in previous systems like H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br].

The vapour-liquid equilibria data obtained for the H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS] system considering the previous parameters are depicted in figure 23.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems



**Figure 23 – Temperature - water fraction diagram for the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS] at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

The *AAD* % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.58%, 0.58 % and 0.59 % respectively, in temperature. Taking into account those values it is concluded that the soft-SAFT EoS is a capable model to describe the vapour-liquid equilibria of the system composed by water + 1-butyl-3-methylimidazolium tosylate.

#### 3.1.6 H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>]

Studying now the vapour-liquid equilibrium of the binary mixture H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] it was considered that water has four associating sites and 1-ethyl-3-methylimidazolium methanesulfonate has three associating sites. The optimized values for the cross-association energy and cross-associating volume, considering the binary parameters equal to one, were 3320 (K) and 2720 (Å<sup>3</sup>) respectively. The value chosen for the associating volume is in the same order than the correspondent values used in the systems: H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>], H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>], H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br]. These values could be seen like a base to study other similar water + ILs systems.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

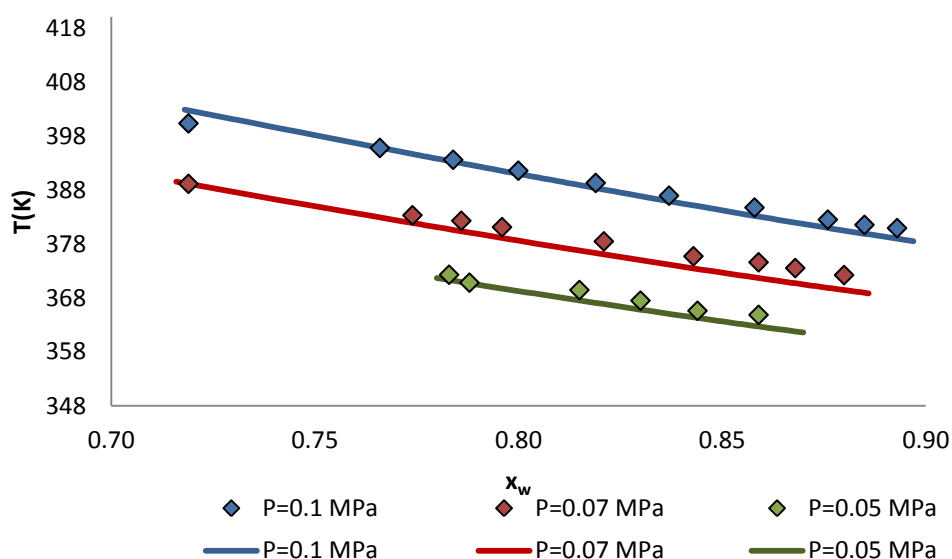
In the same way to what happened in the previous systems, to improve the VLE results it was also necessary to use different binary parameters values for each pressure. The values are depicted on table 4.

**Table 4 - Binary parameters considered for the pressures: 0.1 MPa, 0.07 MPa and 0.05 MPa.**

P(MPa)	$\eta_{ij}$	$\xi_{ij}$
0.101325	1	1.27
0.07	1	1.27
0.05	1	1.25

No change on the  $\eta_{ij}$  value produced VLE results modifications, only changes on the  $\xi_{ij}$  parameter had significant changes on the VLE results. The  $\xi_{ij}$  values used to describe the vapour-liquid equilibria are considerable higher than one and are in the same range as those used on the previous systems. Again, it is noticed that high pressure values require high adjustable binary parameters. This conclusion was also verified for the systems: H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS]. Finally it is visible by the table 4 that the  $\xi_{ij}$  value used to P=0.1 MPa is equal when P=0.05 MPa.

The vapour-liquid equilibrium obtained for the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] system is depicted in figure 24.



**Figure 24 – Temperature - water fraction diagram for the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

The *AAD* % related to the set of values to each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 0.71%, 0.86 % and 0.82 %, respectively, in temperature.

#### 3.1.7 H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN]

Contrary to the previous ionic liquids, the association scheme for the 1-butyl-3-methylimidazolium thiocyanate was previously identified and studied. The respective molecular parameters are presented on table 1 and taken from the work of Pereira et al.<sup>62</sup>

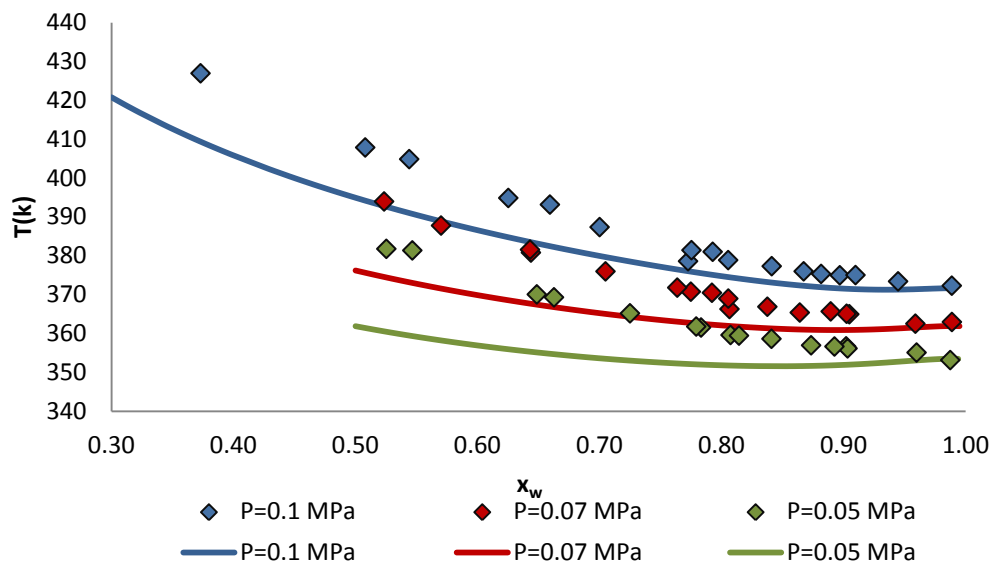
Applying the previous set of values in order to describe the vapour-liquid equilibrium of the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN], the optimized values used for the cross-association energy and the cross-associating volume of the mixture were 3010 (*K*) and 3010( $\text{\AA}^3$ ), respectively. After selecting the best pair of values for the  $k^{HB}$  and the  $\varepsilon^{HB}/k_B$ , that appropriately described the experimental VLE values with binary parameters equal to one, it was began the selection of the best set of these parameters that corrected the deviations in the molecular size and energy of the segments that form the two compounds in the mixture. The purpose is to find the values that improve the modelling results for the three different pressures under study. Nevertheless, and again, it wasn't possible to achieve that goal, and different values for each pressure were necessary. During the calculations it was perceptible that the  $\eta_{ij}$  value can be kept equal to one. The final values of  $\xi_{ij}$  are presented in table 5.

**Table 5 - Binary parameters consider to the pressures: 0.1 MPa, 0.07 MPa and 0.05 MPa.**

P(MPa)	$\eta_{ij}$	$\xi_{ij}$
0.101325	1	1.14
0.07	1	1.12
0.05	1	1.1

Again, it is also visible that the higher the pressure, the higher is the correction necessary to be introduced in the system, traduced by higher  $\xi_{ij}$  values. This is noticed in all the systems that use different binary parameters for each pressure. The final VLE data for the three different pressures are depicted in figure 25.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems



**Figure 25 – Temperature - water fraction diagram for the system H<sub>2</sub>O+ [C<sub>4</sub>mim][SCN] at different pressures. Solid lines represent soft-SAFT EoS results, the experimental results (symbols) were measured by Passos et al.<sup>3</sup>**

Analysing figure 25 it is perceptible that the VLE predictions using the soft-SAFT equation of state follow the same trend of the experimental values proposed by Passos et al.<sup>3</sup>. The *AAD* % related to the set of values for each pressure measured, 0.1 MPa, 0.05 MPa and 0.07 MPa is: 1.7%, 2.1 % and 2.5 % respectively, in temperature.

For all the considered systems, the soft-SAFT EoS is able to describe the increasing of the boiling points values with pressure, and the low pressure influence on the trend of the VLE curves, describing almost parallel T-x curves at the different pressures.

It is important to emphasize that no previous studies were performed where the soft-SAFT EoS was applied to the selected ionic liquids and their aqueous mixtures, and that the association schemes adopted in this work for the ILs should be regarded as initial approaches. The high values for the binary parameters needed, sometimes pressure dependent, and the poor density description found for some of the ionic liquids and their aqueous mixtures suggest that further improvement is required in what concerns the associating schemes proposed for the ionic liquids as well as for their molecular parameters. The COSMOS-RS can be used in future works to assess the proposed ILs association schemes and parameters values.

For some systems the currently available soft-SAFT code is incapable to compute the VLE results for water compositions close to one. That problem is related with numerical issues which cannot be addressed by the thesis author. Nevertheless, the



### **3. Description with the soft-SAFT EoS of the VLE of water + IL systems**

appropriate set of cross-association and binary parameters for the binary systems here considered were already selected from the results of this thesis and can be used when the code problem is solved to complete the calculations in the entire composition range.

### 3. Description with the soft-SAFT EoS of the VLE of water + IL systems

#### 3.2 Resume table

On table 6 all the parameters selected during the VLE study for all the systems analysed during this work are presented.

**Table 6 - Set of parameters selected during the VLE study for the systems here considered.**

	$\eta_{ij}$			$\xi_{ij}$			$\varepsilon^{HB}/k_B$ (k)	$k^{HB}$ ( $\text{\AA}^3$ )
	P=0.1 MPa	P=0.07 Mpa	P=0.05 MPa	P=0.1 MPa	P=0.07 MPa	P=0.05 MPa		
H <sub>2</sub> O+[C <sub>4</sub> mim] [CF <sub>3</sub> SO <sub>3</sub> ]	1	1	1	1.10	1.10	1.10	3292	2585
H <sub>2</sub> O+ [C <sub>4</sub> mim] [CF <sub>3</sub> CO <sub>2</sub> ]	1	1	1	1.17	1.17	1.17	3111	3510
H <sub>2</sub> O+ [C <sub>4</sub> mim] [Cl]	1.18	1.18	1.18	1.27	1.27	1.217	3432	3820
H <sub>2</sub> O+ [C <sub>4</sub> mim] [Br]	1	1	1	1.26	1.24	1.22	3432	3180
H <sub>2</sub> O+ [C <sub>4</sub> mim] [TOS]	1	1	1	1.26	1.26	1.22	2810	2750
H <sub>2</sub> O+ [C <sub>4</sub> mim] [CH <sub>3</sub> SO <sub>3</sub> ]	1	1	1	1.27	1.25	1.25	3320	2720
H <sub>2</sub> O+ [C <sub>4</sub> mim] [SCN]	1	1	1	1.14	1.12	1.10	3010	3010

## **4. Description of water activity coefficients of water + ILs systems with the soft-SAFT EoS**



## 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

### 4.1 Introduction

For an adequate choice or design of ionic liquids, the knowledge of their interaction with other solutes and solvents is an essential feature for predicting the reactivity and selectivity of systems involving these compounds, during this chapter it will be presented the activity coefficients of systems composed by water and the ionic liquids studied above using the soft-SAFT EoS. The soft-SAFT equation is here used for the first time to describe activity coefficients.

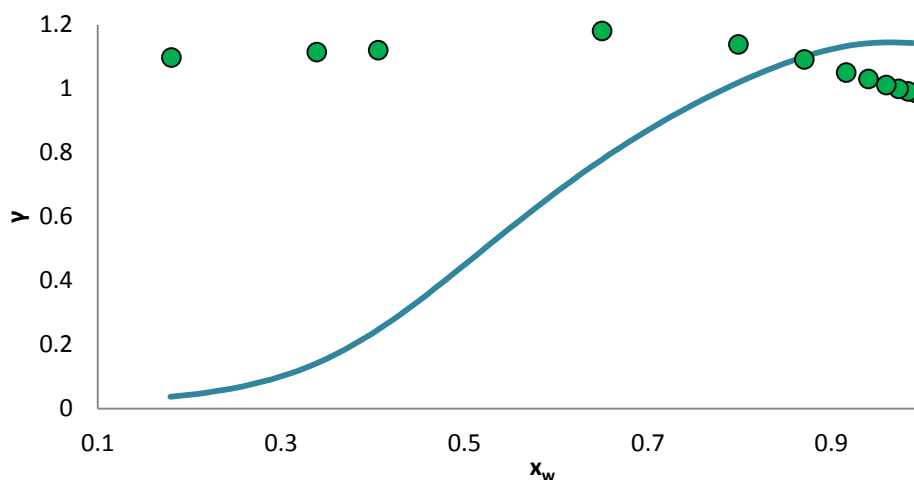
After the selection of the association scheme and then the molecular parameters optimization, following the vapour-liquid equilibria description it is now possible the description of the activity coefficients of water in several imidazolium-based ionic liquids with the common cation 1-butyl-3-methylimidazolium. The systems were studied at 298.2 *k* and are the following: H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>], H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>], H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl], H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br], H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS], H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN]. The activity coefficients analysis is the final step that allows the selection of the best pair composed by water and ionic liquid. This final conclusion will be used in one of the many ILs applications, namely in absorption refrigeration systems.

### 4.2 Activity coefficients

#### 4.2.1 H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>]

In order to determine the applicability of these systems (water + ILs) the activity coefficients were determined using the soft-SAFT EoS. In figure 26 are depicted the water activity coefficients for the system composed by water and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, both the soft-SAFT modelling results and the experimental data<sup>60</sup>.

#### 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS



**Figure 26 - Activity coefficients to the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>]. Solid lines represent the soft-SAFT EoS results and the symbols the experimental data<sup>60</sup>, measured at 298.2 K.**

Analysing figure 26 it is perceptible that the results produced by soft-SAFT EoS diverge from the data measured by Khan et al.<sup>60</sup> what is confirmed by the AAD %, that is about 31.8 %. The information given and used to compute with (soft-SAFT) the activity coefficients are the molecular parameters optimized for each pure compound from density data, the cross association energy and volume parameters and the size and energy binary interaction parameters. No information based on the activity coefficients data is introduced in the regression of these parameters. A potential solution to improve the results can be the introduction of more data like activity coefficients information, during the molecular parameters optimization, since just density data were used in this work. A similar study was made by Passos et al.<sup>3</sup>, she described the activity coefficients of several water + IL systems using the PC-SAFT, and also considered activity coefficients data during the parameters optimization. It is also important to note that it is the first time that these ionic liquids are under study, thus the association scheme proposed during this work could not be the best option, and then different association schemes must be analysed in future works, as already discussed.

The experimental values measured by Khan et al.<sup>60</sup> show weak interactions between the water and this ionic liquid due to activity coefficients larger than the unity in a wide range of concentrations, contrary to the results obtained from soft-SAFT.

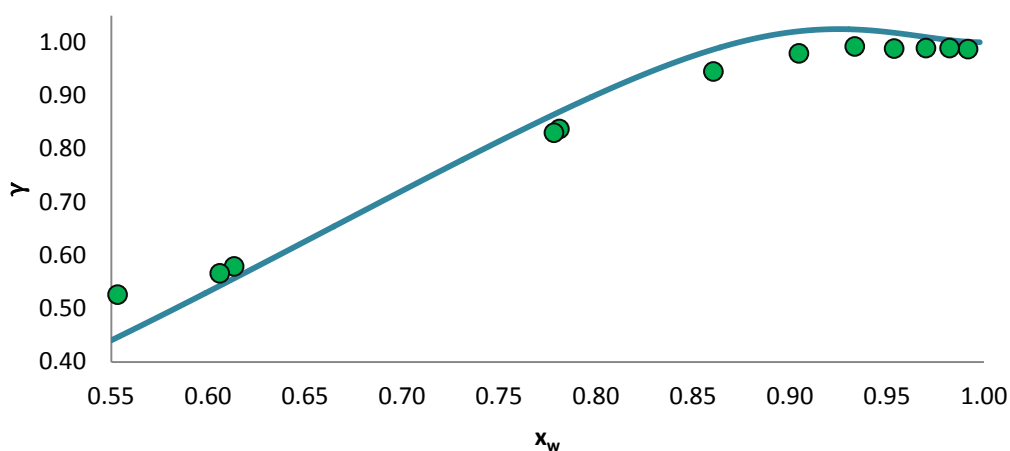
As depicted on figure 26 the soft-SAFT shows problems when describing the water activity coefficients of this system. Khan et al.<sup>60</sup> used the COSMO-RS to describe the water activity coefficients of the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>] system and in a similar way as

#### 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

happens in this work, the model used wasn't able to describe the experimental data<sup>60</sup>.

##### 4.2.2 H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>]

The preceding approach was also applied to other system, this one composed by water and 1-ethyl-3-methylimidazolium trifluoroacetate. The results are depicted in figure 27.



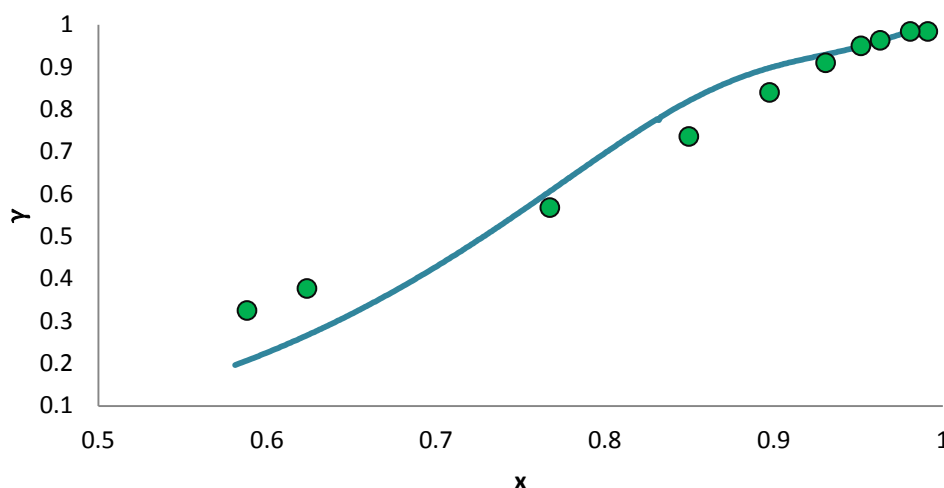
**Figure 27 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>]. Solid lines represent the soft-SAFT EoS results and symbols the experimental data<sup>60</sup>, measured at 298.2 K.**

As depicted in figure 27 the soft-SAFT EoS is capable to predict the water activity coefficients of the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>] system, the results are very similar to the experimental values measured by Khan et al.<sup>60</sup>, and contain an AAD % of only 4.46, which represents a good result. The soft-SAFT EoS is able to describe the experimentally observed values of activity coefficients, which characterize stronger interactions between the water and the ionic liquid. The maximum activity coefficient value is attained at  $x_w=0,93$ . Comparing the two systems already presented, H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>], it is evident that the presence of the acetate causes a decrease in the water activity coefficient which is related to stronger interactions between the water and the ionic liquid present. Besides being able to take into account these stronger interactions, soft-SAFT is also capable to describe the nonmonotonic behaviour of the water activity coefficients in the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>] system, particularly for high ionic liquid concentration solutions.

## 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

### 4.2.3 H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>]

The following system considered is composed by water and 1-ethyl-3-methylimidazolium methanesulfonate, in figure 28 it is presented the activity coefficients computed by soft-SAFT EoS for this system, as well as the correspondent experimental data<sup>60</sup>.



**Figure 28 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>]. Solid lines represent the soft-SAFT EoS results and symbols the experimental data<sup>60</sup>, measured at 298.2 K.**

Analysing figure 28 it is noticeable that the data obtained by soft-SAFT EoS are in line with the activity coefficient values experimentally measured by Khan et al.<sup>60</sup> and present an AAD of 12.2 %.

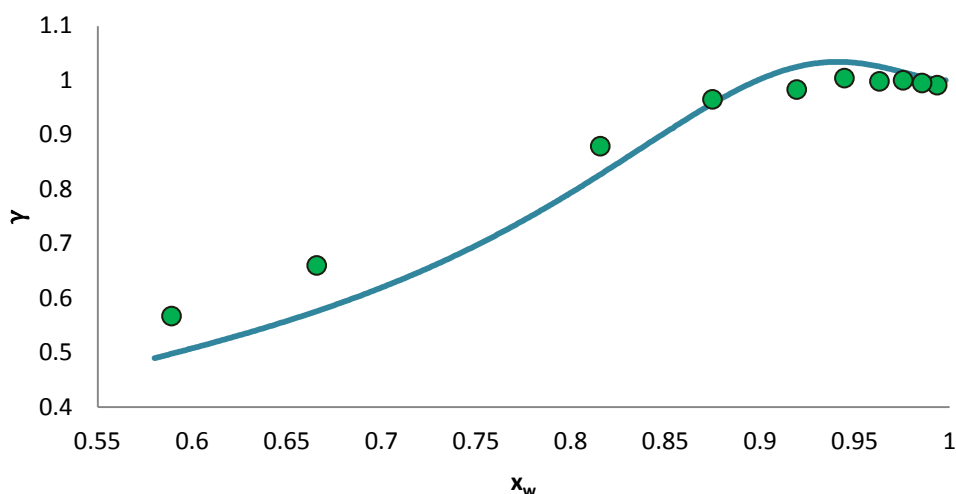
As for the other system, H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>], also here the interactions between the water and the 1-ethyl-3-methylimidazolium methanesulfonate seem to be strong, since the IL under study presents water activity coefficients lower than one, a behaviour well predicted by the model here considered. Comparing the systems H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>SO<sub>3</sub>] and the H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] and analysing the values measured by Khan et al for both cases, it is visible that the fluorination of the anion causes a decrease on the interactions between the water and the ionic liquid, that is traduced by water activity coefficients larger than the unity (positive deviation to ideality) in a wide range of concentrations. The lack of fluorination and the consequently stronger water-ionic liquids interactions in the system H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] are well taken into account by the soft-SAFT EoS.



## 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

### 4.2.4 H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS]

The next system that was studied is composed by water and the ionic liquid 1-ethyl-3-methylimidazolium tosylate. The set of values produced by soft-SAFT EoS are represented in figure 29.



**Figure 29 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [TOS]. Solid lines represent the soft-SAFT EoS results and symbols the experimental data<sup>60</sup> measured at 298.3 K.**

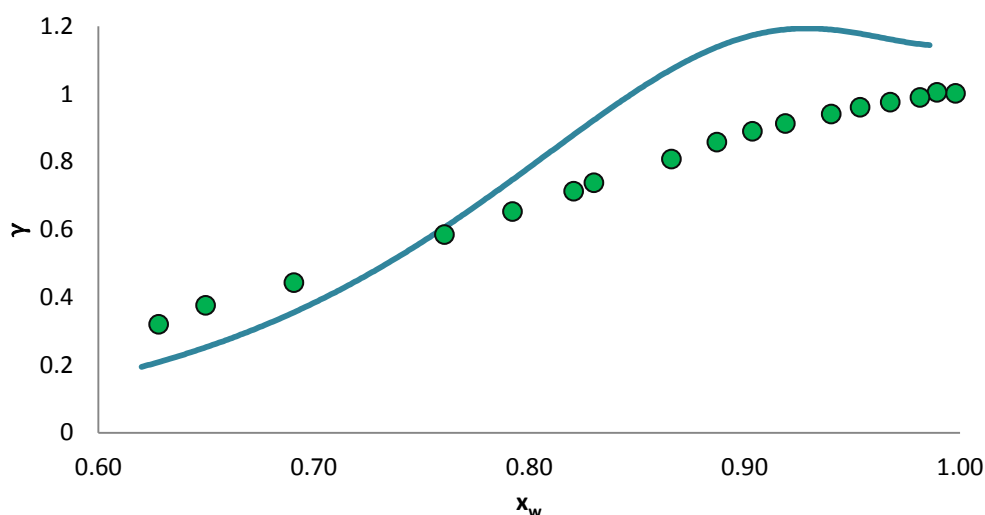
Based in figure 29 it is visible that the set of values given by the soft-SAFT EoS are in line with the experimental data measured by Khan et al.<sup>60</sup>, the associated AAD % is of 4.56 %, this value showing the good agreement between the two set of values. This behaviour is also confirmed in other systems like: H<sub>2</sub>O+ [C<sub>4</sub>mim] [CF<sub>3</sub>CO<sub>2</sub>] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>]. The maximum value is obtained for  $x_w = 0.941$ .

Comparing the figures 28 and 29 it can be studied the effect of substituting -CH<sub>3</sub> in [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>] with an aromatic ring, as in the case of [C<sub>4</sub>mim] [TOS]. The results show that the phenyl group decreases the interaction with water as expressed by the increase in the water activity coefficient when compared to that of [C<sub>4</sub>mim] [CH<sub>3</sub>SO<sub>3</sub>], behaviour which is well predicted with the soft-SAFT EoS.

## 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

### 4.2.5 H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl]

The final three systems studied during this thesis are the H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl], H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br] and H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN], all these systems have in common the fact that were all modelled considering four associating sites in water and one in the ionic liquid. In this section it will be presented the activity coefficients study performed for the system composed by water and 1-ethyl-3-methylimidazolium chloride. The set of values achieved by soft-SAFT EoS are depicted on figure 30.



**Figure 30 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl]. Solid lines represent the soft-SAFT EoS results and symbols the experimental data<sup>60</sup> measured at 298.2 K.**

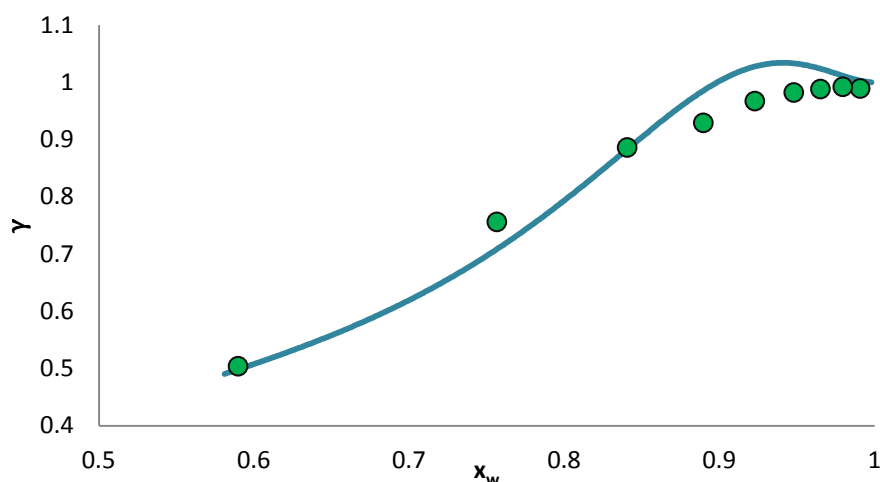
As presented on figure 30 the soft-SAFT seems to be a good tool to describe the water activity coefficients of this system for low concentrations, since around  $x_w \approx 0.8$  the results predicted by soft-SAFT start to show a different behaviour, and start to spread apart from the experimental values measured by Khan et al.<sup>60</sup> The AAD % present on the results predicted by soft-SAFT is about 19.7 %, this number demonstrates the discrepancy between the two set of results present on figure 30. Despite this conclusion, the model results continue to present low activity coefficients values in most of the concentration range, which indicate strong interactions between the water and the ionic liquid, as observed experimentally. These results must be improved, one way is to use activity

#### 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

coefficients data during the calculations the parameters regression, as previously suggested.

##### 4.2.6 H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br]

One of the last systems that will be here studied is the H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br], in figure 31 are presented the two set of values for the activity coefficients, the values achieved using the soft-SAFT and the experimental values.



**Figure 31 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br]. Solid lines represent the soft-SAFT EoS predictions and symbols the experimental data<sup>60</sup> measured at 298.2 K**

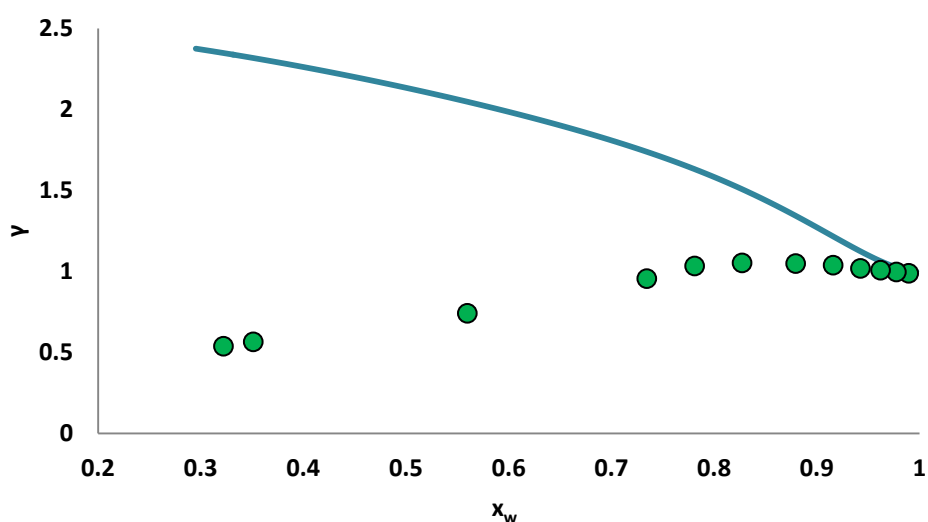
Observing figure 31 it is possible to conclude that the water activity coefficients predict by soft-SAFT are in agreement with the experimental values measured by Khan et al.<sup>60</sup>, however it is visible a mismatch between the two sets when the water concentration is high. The AAD % present on the data obtained by the model is about 3.76 %, this value evidences that the soft-SAFT EoS is a tool that produce good results when applied for this system. Based on figure 31 it is concluded that the interactions between the water and the 1-ethyl-3-methylimidazolium bromide are strong, but not in all the concentration range as happened with the previous system studied. This conclusion is based on the lower activity coefficients values produced by soft-SAFT EoS and in agreement with the experimental data. Comparing now the systems where the ionic liquid was modelled with one associating site, the H<sub>2</sub>O+ [C<sub>4</sub>mim] [Cl] and the H<sub>2</sub>O+ [C<sub>4</sub>mim] [Br], it is perceptible from figures 30 and 31, that water has strong interactions

#### 4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS

with both ILs. Which is indicated by the low water activity coefficients, being lower for [C<sub>4</sub>mim] [Cl] than for [C<sub>4</sub>mim] [Br]. The increase in size and respective decrease in charge density of the bromide in comparison with the chloride results in a weaker interaction of the [C<sub>4</sub>mim] [Br] with water. The same conclusion is achieved comparing the values produced by soft-SAFT for both cases.

##### 4.2.7 H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN]

Finally it will be presented the H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN] system. The activity coefficient results are presented on figure 32.



**Figure 32 - Activity coefficients of the system composed by H<sub>2</sub>O+ [C<sub>4</sub>mim] [SCN]. Solid lines represent the soft-SAFT EoS results, and symbol the experimental data<sup>60</sup> measured at 298.2 K.**

Through figure 32 it is noticed that the results produced by the soft-saft EoS are quantitatively different from the values measured by Khan et al.<sup>60</sup> The AAD associated to these results is of 89.5 %. On the contrary to the experimental data, these results indicate that the water activity coefficients are larger than unity (positive deviation to ideality) in the whole range of concentrations. The experimental data show weak interactions with [C<sub>4</sub>mim] [SCN] and water because the system presents water activity coefficients larger than unity (positive deviation to ideality) in a wide range of concentrations but not in the entire range as predicted with soft-SAFT. The soft-SAFT results behaviour presented in figure 32 was also identified in a previous work<sup>60</sup> using the COSMOS –RS. In that work that model was also incapable to quantitative describe the water activity coefficients of

#### **4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS**

this system, in fact the results provided with the COSMOS-RS are very similar in values and in curve shape to the ones presented here with soft-SAFT EoS.

Nevertheless, and as obtained with the COSMOS-RS model, the soft-SAFT EoS results are qualitatively correct by identifying a positive deviation to ideality in this system. As already said, this system is here studied for the first time, so all the work applied to each IL can be done in a different way, trying new association schemes or new molecular parameters. Using water activity coefficients data is a possibility to improve the final results.

#### **4. Description of water activity coefficients of water +ILs systems with the soft-SAFT EoS**

## **5. Conclusions**





## 5. Conclusions

In order to improve the performance of the ionic liquids in one of the many applications that the ILs are able to, namely as new cooling absorbents for absorption chillers or absorption heat pumps where one possible working pair might be composed of water (refrigerant) and IL (absorber), where studied in this work 7 systems composed by water and IL, they ILs are :  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{SO}_3]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{CO}_2]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Cl}]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Br}]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{TOS}]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CH}_3\text{SO}_3]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{SCN}]$ . These systems were studied here for the first time using the soft-SAFT EoS.

To achieve the goal of this work some studies were done. Initially association schemes for the ionic liquids were proposed, and then, using density data molecular parameters were optimized. Following the vapour-liquid description, the soft-SAFT shows a strong capability to describe the VLE data. Excellent results were obtained for the systems:  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{SO}_3]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{CO}_2]$ ,  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Cl}]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Br}]$ .

Finally the water activity coefficients of the several systems were studied. It was the first time that soft-SAFT EoS was applied to describe this property. The results are in concordance with the experimental results except for the systems:  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CF}_3\text{SO}_3]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{SCN}]$ . It was concluded that the ionic liquids that have stronger interactions with water are the  $[\text{C}_4\text{mim}] [\text{CH}_3\text{SO}_3]$  and the  $[\text{C}_4\text{mim}] [\text{Cl}]$ , these two ILs show activity coefficients lower than the unity in wide concentrations ranges. It was also verified by the values produced by soft-SAFT EoS that the ionic liquid with weaker interactions with water is the  $[\text{C}_4\text{mim}] [\text{SCN}]$ , the system  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{SCN}]$  presents water activity coefficients larger than unity in a wide range of concentrations.

A potential pair to be used in absorption processes should show a larger boiling temperature elevation and/or vapour pressure depression. The boiling-temperature elevation of water depends on the kind of IL, on the IL concentration in the mixture and on temperature. For this application low activity coefficient values are desired, meaning strong water- IL interactions. The pairs that satisfy these conditions are the:  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{CH}_3\text{SO}_3]$  and the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}] [\text{Cl}]$ .

It is important to remember that systems containing water and this set of ionic liquids were here presented and studied for the first time with soft-SAFT EoS.

## 5. Conclusions

## **6. Future Work**



## 6. Future Work

With the goal to optimize the ILs applications, in specific, the use of ionic liquids in the cooling absorbent area, some work is still needed to be completed in the future. The vapour-liquid equilibrium and water activity coefficients study, introducing activity coefficients data during the parameters regressions, will be an appropriate analyse that should be done with soft-SAFT EoS for the systems for which this model wasn't able to properly describe at the same time the VLE data and the water activity coefficients information.

Other investigation that should be performed is the study of the best association scheme for the ILs using the COSMOS-RS.

## 6. Future Work

## **7. References**





## 7. References

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## **8. Appendix**





**Appendix A- Molecular Parameters****Table 7 - Molecular parameters optimized for the ionic liquids.**

	$m$	$\sigma$	$\varepsilon/k_B$	$\varepsilon^{HB}/k_B$	$k^{HB}$	%AAD
[C <sub>4</sub> mim][CF <sub>3</sub> SO <sub>3</sub> ]	5.073	3.602	148.0	3700	5886	4.488
[C <sub>4</sub> mim][TOS]	4.809	4.385	380.6	3580	5515	0.076
[C <sub>4</sub> mim][CF <sub>3</sub> CO <sub>2</sub> ]	5.154	3.617	157.9	3700	6004	2.180
[C <sub>4</sub> mim][CH <sub>3</sub> SO <sub>3</sub> ]	6.232	5.810	273.4	3700	2832	0.718
[C <sub>4</sub> mim][Cl]	5.617	4.499	370.1	3699	2305	0.004
[C <sub>4</sub> mim][Br]	5.216	4.313	438.0	2747	2000	0.718

