Modeling the vapor–liquid equilibria and water activity coefficients of alternative refrigerant-absorbent ionic liquid–water pairs for absorption systems

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ABSTRACT

The aim of this study is to describe the phase equilibrium behavior of aqueous solutions of selected ionic liquids (ILs) as new potential pairs of absorption cooling systems. The ILs under study have a shared cation, 1-butyl-3-methylimidiazolium, [C$_4$mim]$^+$, and the following anions: methanesulfonate, [CH$_3$SO$_3$]$^-$, trifluoromethanesulfonate, [CF$_3$SO$_3$]$^-$, acetate, [CH$_3$CO$_2$]$^-$, trifluoroacetate, [CF$_3$CO$_2$]$^-$, tosylate, [TOS]$^-$, bromide, [Br]$^-$, and thiocyanate, [SCN]$^-$.

Each binary system was individually studied within the soft-SAFT framework. A mesoscopic simple molecular model was proposed for each IL, being characterized by a specific set of molecular parameters. In combination with one or, in some cases, two additional binary parameters, it was possible to simultaneously describe the vapor–liquid equilibrium (VLE) of the aqueous binary systems at three different pressures (0.10 MPa, 0.07 MPa and 0.05 MPa) and the correspondent isothermal water activity coefficients at 298.15 K, correctly incorporating the different deviations from ideality and water interactions characteristics for each IL. Infinite dilution coefficients were also predicted in reasonable agreement with the experimental data.

The simple model used with soft-SAFT to represent ILs provides an overall good description of most of the systems. Results for particular systems showed some space for improvement, nevertheless at expense of increasing the model complexity by changing the originally proposed molecular model.

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1. Introduction

Absorption refrigeration technology has, in recent times, attracted considerable research focus due to being environmentally beneficial by making good use of average energy. Common use appliances such as absorption heat pumps and absorption chillers allow a reduction of energy consumption and greenhouse gases emissions, with the consequent environmental benefits [1], while operating with a small quantity of thermic energy originated from sun power or heat produced from industrial waste.

The efficiency of these devices is built upon the thermodynamic properties of the used working pairs. These working pairs are constituted by a refrigerant and an absorbent. Generally, these binary pairs are composed of aqueous mixtures of ammonia or lithium bromide, NH$_3$ and LiBr, respectively [1]. However, their knowable shortcomings (toxicity, apparatus deterioration, crystals formation and poor thermal stability) restrain their industrial use, driving the search for alternative working pairs.

Considering the handicaps of commonly used refrigeration pairs, ionic liquids (ILs) have appeared as possible novel types of absorbents for absorption chillers or heat pumps, based on their negligible volatility and elevated, in some cases, hydrophilicity. Also, recent research studies have shown their null or very low toxicity at short alkyl chain cation lengths [2], to which the anion seems to have low influence [3]. In addition, the range of thermal stability of ILs can reach over 400 °C [4]. Further considerations can be established for particular cases, such as the imidazolium cations, which are particularly stable, with the thermal stability increasing with the anion size [5], while decreasing for halide anions [6].

Understanding the phase equilibria and thermodynamic properties of binary aqueous solutions of ILs is essential to establish

them as alternatives to the common working pairs used in absorption heat pumps and absorption chillers. With this purpose, numerous literature works have been published: Kim et al. [7] were the first authors to measure and study the vapor pressures of aqueous ILs for the systems water + 1-butyl-3-methylimidazolium bromide ($[C_4mim][Br]$), water + 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4C_1im][BF_4]$) and water + 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ($[OHC_2mim][BF_4]$) in a wide concentration and temperature ranges using the boiling-point method. Zuo et al. [8] proposed the system water + 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2mim][C_2H_5SO_4]$) as a new working pair. In their work, the mixture vapor pressure, heat capacity and density were experimentally determined and theoretically described using the NRTL approach to calculate the vapor pressures and simple polynomial functions of temperature and molar fraction to correlate heat capacities and densities. No comparison with other working pair properties was carried out in that work. Wang et al. [9] proposed the use of the mixture composed by water and 1,3-dimethylimidazolium chloride ($[C_1mim][Cl]$) based on vapor pressures and water activity coefficients experimental measurements. They concluded that the water + $[C_1mim][Cl]$ pair can be an encouraging substitute working set to enhance the absorption cooling cycle efficiency due to the strong affinity between the two compounds seen through the low water activity coefficients values. Zhang et al. [10] replicated one absorption cycle using the water + 1,3-dimethylimidazolium dimethylphosphate ($[C_1mim][Me_2PO_4]$) pair and compared the results with those of the solution H_2O + LiBr. They concluded that this new working pair has a comparable performance with that of the typical H_2O + LiBr mixture. Kim et al. [11] presented a comprehensive theoretical study on several refrigerants and ILs systems as working pairs for absorption refrigeration systems, and found that the circulation ratio is affected by the refrigerants solubility in the ILs, as well as by its temperature dependency. These authors also recommended that cations having shorter alkyl chains should be preferred due to a superior sensitive temperature dependency of the solubility. Wu et al. [12] measured vapor pressures and the vapor−liquid equilibrium (VLE) of water and 1,3-dimethylimidazolium tetrafluoroborate ($[C_1mim][BF_4]$) mixtures and proposed them as favorable working pairs when comparing with $[C_1mim][Cl]$ and $[C_4mim][BF_4]$. Nie et al. [13] measured the thermodynamic properties of the water + 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[OHC_2mim][Cl]$) mixture, including vapor pressures, densities and heat capacities. They suggested this binary mixture as a novel alternative working pair for the absorption heat pump cycle. Recently, Carvalho et al. [14] measured the VLE of 1-ethyl-3-methylimidazolium chloride ($[C_2mim][Cl]$), 1-butyl-3-methylimidazolium chloride ($[C_4mim][Cl]$), 1-hexyl-3-methylimidazolium chloride ($[C_6mim][Cl]$) and choline chloride ($[N_{11}(2OH)][Cl]$) with water and ethanol using a novel isobaric micro-ebulliometer at pressures from 0.05 to 0.1 MPa. They found that some of the working pairs could be suitable for absorption chillers or absorption heat pumps, since they present negative deviations from Raoult's Law.

Besides the experimental measurements and empirical correlations, theoretical based thermodynamic models have been used and developed to describe the thermodynamic properties and phase equilibria of IL solutions with water: Wang et al. [15] used the Square-Well Chain Fluid with Variable Range EoS (SWCF-VR) to describe the VLE of several systems constituted by water + bis(trifluorosulfonyl)imide [Tf_2N]-based ILs. The imidazolium-based ILs were modeled as di-block square-well chains, being one block the substituent alkyl group and the other one the imidazolium ring-anion. The equation parameters for the imidazolium anion were determined through fitting to available

experimental pressure-volume-temperature (pVT) information, and no cross-association with water was explicitly taken into account. Banarjee et al. [16] successfully used the Conductor-like Screening Model for Realistic Solvation (COSMO-RS), a predictive model grounded on unimolecular quantum chemistry computations, to predict the VLE of water + alkylimidazolium-based ILs. The model was also able to describe the low and high boiling azeotrope formation. Freire el el. [17,18], investigated the VLE and the LLE of several water + IL mixtures with COSMO-RS. The VLE predictions captured the behavior of the existing experimental data, satisfactorily reproducing all the ILs structural changes in their phase behavior. Yet, for the LLE predictions, some handicaps of the model were observed, particularly for the anions influence. Carvalho et al. [14] applied the NRTL model to compute the VLE data of binary systems of water/ethanol + IL and the non-ideal behavior of the IL phase solutions. A good fit of the experimental VLE data was obtained, showing the NRTL model suitability for the initial design of extractive distillation processes.

The complex nature of water and ILs, strongly influenced by the hydrogen bonding and other short-range directional attractive forces, suggests the need for a model where these effects could be explicitly considered. In this direction, the use of the Statistical Association Fluid Theory (SAFT) and its subsequent variants seems a promising route for an accurate modeling of those systems. SAFT-type equations of state (EoSs) are theoretically based on Wertheim's first-order thermodynamic perturbation theory [19–21], differing on the choice of the reference fluid. The original version was proposed by Chapman et al. [22] applying a hard-sphere for the reference fluid. Among many variants, the most popular and utilized since their development are the SAFT-VR [23] (using a square-well with a variable range as a reference potential), the soft-SAFT [24,25], (using a Lennard-Jones reference fluid) and the PC-SAFT [26] (applying the perturbation over a hard-chain as a reference). The choice of the equation as applied to experimental systems depends on the searched accuracy which, conversely, depends on the systems under study and the availability of the code to do the calculations.

SAFT-type EoSs have also been used to study water + ILs systems. Paduszynski and Domanska used PC-SAFT to calculate the liquid−liquid equilibrium (LLE) and the solid−liquid equilibrium (SLE) of several water + IL mixtures [27]. Independently of the anion, the authors modeled the ILs using 10 association sites to represent the cation−anion interactions. Binary corrections were adjusted to infinite dilution activity coefficients of a particular solute in a given IL, either determined experimentally or predicted by means of the modified UNIFAC group contribution method. More recently, the same research group has published another contribution where PC-SAFT was used to model the VLE, enthalpy and molar heat capacity data of ethylsulfate-based [$EtSO_4$]$^−$ ILs with water [28]. Based on the amount of lone pairs present in the cation and the anion, they suggested a model with up to 14 associating sites. Passos et al. [29] experimentally measured the VLE at reduced pressures of water + imidazolium-based ILs and also used the PC-SAFT equation to describe the experimental data. The IL molecular parameters (following a 2B scheme for association) and a binary interaction parameter were determined by a simultaneous regression of pure-IL densities, water activity coefficients at 298.15 K and VLE data at 0.1 MPa. While a cross-association model was established, the energy of self-association of all ILs showing negative deviations respect to ideality was set to zero. In two additional contributions from Held and co-workers, ternary mixtures involving water and ILs were successfully modeled with the same equation. In the first work [30], the LLE data for 1-butanol, water and several ILs were described trying different approaches to fit the binary interaction parameters, being able to predict the sensitive

distribution coefficient and the selectivity of 1-butanol. In a second recent work [31], PC-SAFT has been used to predict the three-phase behavior of (water + [C$_{10}$mim][Tf$_2$N] + n-dodecane) and (water + [C$_{12}$mim][Tf$_2$N] + n-dodecane) ternary systems at 298.15 K and atmospheric pressure without any fitting parameter. In another recent contribution, Shahriari et al. [32] have combined PC-SAFT with the Mean Spherical Approximation (MSA) theory to describe the formation of ions in aqueous ILs solutions. Modeling the ILs as chain electrolytes with adjusted ion parameters, they have calculated the osmotic coefficients, mean ionic and water activity coefficients, liquid densities and the apparent molar volume of several ILs, in good agreement with experimental data.

In the recent years, Vega and co-workers have successfully applied the soft-SAFT EoS [24,25,33], to describe the phase equilibria of several water + ILs systems. The VLE of water + [C$_n$mim][Tf$_2$N] mixtures was predicted and the LLE was very well correlated with this equation [34], finding excellent agreement with the experimental data. Similar results were obtained when describing the LLE of water + [Tf$_2$N] pyridinium ILs using no more than one binary interaction parameter for each system [35]. The [C$_n$mim][PF$_6$] + water family was also very well described with the soft-SAFT EoS with one temperature and chain-length independent binary parameter [36]. In a very recent contribution [37], the water + [C$_n$mim][BF$_4$] family was used as an example to highlight the ability of soft-SAFT to provide useful information by transferring the binary interaction parameter used to describe the VLE of aqueous [C$_4$mim][BF$_4$] for the prediction of the LLE of [C$_6$mim][BF$_4$] and [C$_8$mim][BF$_4$] in water. Other properties, such as the excess enthalpy and the viscosity of the mixture, were also predicted in very good agreement with the experimental data.

In this context, the main objective of this work is to extend these studies to access new possible working pairs (water + ILs), which could be used as alternative refrigerant-absorbent pairs for absorption systems, addressing ILs from the cation family 1-butyl-3-methylimidiazolium with different anions of variable hydrophilicity. The soft-SAFT EoS is used to describe the VLE and isothermal water activity coefficients of these systems.

The paper is organized as follows: after a short description of the theoretical approach and the equations used for the calculation of different thermodynamic properties, a reliable but yet simple molecular model is proposed for each IL, defining number and type of associating sites. Once the molecular parameters for the pure ILs are determined, the VLE and water activity coefficients of the ILs binary mixtures at different conditions are calculated and compared to experimental data. A discussion of the accuracy and limitations of the model is also presented. A summary of conclusions is provided at the end of the paper.

2. Theory

In a similar way as all other SAFT equations, soft-SAFT is presented as an addition of contributions to the Helmholtz energy of the system [24,25]:

$$\frac{A^{total}}{Nk_BT} - \frac{A^{ideal}}{Nk_BT} = \frac{A^{res}}{Nk_BT} = \frac{A^{ref}}{Nk_BT} + \frac{A^{chain}}{Nk_BT} + \frac{A^{assoc}}{Nk_BT} \tag{1}$$

The Lennard-Jones (LJ) spherical fluid is used to account for the attractive and repulsive interactions of the monomers taking part of the chain. To extend it to mixtures, the van der Waals one-fluid theory with the generalized Lorentz−Berthelot (LB) combining rules (see Eqs. (2) and (3)) for the size σ_{ii} and energy ε_{ii} parameters are applied:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\varepsilon_{ij} = \xi_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{3}$$

The binary parameter ξ_{ij} accounts for deviations on the cross-dispersive energy between different molecules with respect to the original LB rule (given when $\xi_{ij} = 1$, which means the mixture is predicted from the pure component parameters). This parameter is typically fitted to experimental data of binary mixtures.

The only requirement to extend the association treatment to mixtures is the evaluation of the cross-association values of the volume (κ_{ij}^{HB}) and energy ($\varepsilon_{ij}^{HB}/k_B$) to account for the volume and energy of association between different compounds. The mean arithmetic of the radius of the associating site r_c for κ_{ij}^{HB} and the modified geometric average for $\varepsilon_{ij}^{HB}/k_B$ (in a comparable way as it is carried out for σ_{ij} and ε_{ij}/k_B) are used with the soft-SAFT to obtain these values:

$$\kappa_{ij}^{HB} = \left(\frac{\sqrt[3]{\kappa_{ii}^{HB}} + \sqrt[3]{\kappa_{jj}^{HB}}}{2}\right)^3 \tag{4}$$

$$\varepsilon_{ij}^{HB} = \alpha^{HB}\left(\varepsilon_{ii}^{HB}\varepsilon_{jj}^{HB}\right)^{1/2} \tag{5}$$

It is important to remark that a binary parameter, α^{HB}, has been added to Eq. (5) so as to account for a correction of the cross-association energy value different that the one predicted by the combining rule, in case the predictions from pure component parameters provide inaccurate results.

With soft-SAFT, associating compounds are described with five molecular parameters: the chain length, m_i, the segment diameter, σ_{ii}, the dispersive energy between segments, ε_{ii}/k_B, the bonding volume, κ_{ij}^{HB}, and the energy of association, $\varepsilon_{ij}^{HB}/k_B$.

The calculation of the activity coefficients is also given as a quantitative measure to check deviations from the ideal behavior of these mixtures. The procedure followed here is done in a similar manner to calculations with other SAFT-type EoSs [29]. In particular, water activity coefficients, γ_{H2O}, are evaluated from standard thermodynamic relations, as the ratio of the water fugacity coefficient at the mole fraction in a mixture, and the fugacity coefficient of the pure water:

$$\gamma_{H2O}(T,P,x_{H2O}) = \frac{\varphi_{H2O}^L(T,P,x_{H2O})}{\varphi_{0,H2O}^L(T,P,x_{H2O}=1)}, \tag{6}$$

where φ is the fugacity coefficient of water. A particular case of Eq. (6) is the calculation of infinite dilution coefficients, when the mole fraction of water approaches zero:

$$\gamma_{H2O}^\infty(T,P,x_{H2O}) = \frac{\varphi_{H2O}^{\infty,L}(T,P,x_{H2O}\to0)}{\varphi_{0,H2O}^L(T,P,x_{H2O}=1)} \tag{7}$$

Eqs. (6) and (7) can be further simplified considering that the volatility of the ILs studied here is negligible (vapor phase will be pure water) and that the working pressure is low (vapor fugacity coefficients very close to unity):

$$\gamma_{H2O}(T,P,x_{H2O}) = \frac{P}{x_{H2O}P_{H2O}^{sat}(T)}, \tag{8}$$

where P^{sat} is the saturation pressure of pure water at the working temperature.

3. Results and discussion

3.1. Molecular models

The first step to apply any SAFT to experimental systems is to propose the molecular models of the different compounds, specifying the number and type of associating sites in the case of associating fluids. Strong efforts have been undertaken in recent years to establish appropriate molecular models for different families of ILs, based on different approaches and available information. Soft-SAFT modeling of ILs is grounded on the hypothesis of a low ionic character of the IL, with their ions interacting through dispersion forces, explicit steric interactions and the creation of short-lived ion pairs [38], resulting in considering ILs as single chain molecules with the cation and the anion together and with an anisotropic interaction between the different pairs, taken into account through assigned association sites. As explained in earlier publications [39,40], the model is built also using quantum information and molecular simulation results as guides. In spite of its simplicity, this simple model has proved to be accurate for several experimental systems [39,40].

The imidazolium cation [C$_n$mim] IL family has been the most studied, while the anions vary in their forms. In the pioneering work of Andreu and Vega [39], they modeled the [C$_n$mim][BF$_4$] and the [C$_n$mim][PF$_6$] ionic liquids as LJ chains with one associating site. This model was used in the following years to compute gases solubilities and the phase equilibria of ILs binary mixtures and aqueous systems [36,39], in very good agreement with the experimental data. The same approach was followed by Mac Dowell et al. [41] for the [C$_4$mim][Cl] in 2014.

Based on the charge distribution, ILs formed by the bis(trifluorosulfonyl)imide [Tf$_2$N]$^-$ anion coupled with imidazolium and pyridinium cations were described within the soft-SAFT approach with three associating sites [34,35,40]. The same choice was given for the dimethylphosphate, [Me$_2$PO$_4$]$^-$, [C$_n$mim] family [41]. The imidazolium methylphosphonate, [CH$_3$OHPO$_2$]$^-$, ionic liquid was represented as a LJ chain with two associating sites [42]. Finally, in the last couple of years, the cation [C$_4$mim]$^+$ with the anions thiocyanate, [SCN]$^-$, dicyanamide, [N(CN)$_2$]$^-$, acetate, [CH$_3$CO$_2$]$^-$, and methyl sulfate, [MeSO$_4$]$^-$, were also addressed, being modeled with one or two associating sites [43–45], depending on the particularities of each anion.

In this work, we present molecular models for five [C$_4$mim] ILs with different anions using the soft-SAFT EoS: 1-butyl-3-methylimidazolium methanesulfonate ([C$_4$mim][CH$_3$SO$_3$]), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C$_4$mim][CF$_3$SO$_3$]), 1-butyl-3-methylimidazolium trifluoroacetate ([C$_4$mim][CF$_3$CO$_2$]), 1-butyl-3-methylimidazolium tosylate ([C$_4$mim][TOS]) and 1-butyl-3-methylimidazolium bromide ([C$_4$mim][Br]). Following the same approach used in earlier works, a molecular model was proposed for each of them, based on appropriate association schemes. For [C$_4$mim][CF$_3$SO$_3$], three associating sites were considered: one association site A standing for the O$^-$ atom interactions with the cation and two association sites B for the delocalized charge due to the additional oxygens. A similar association scheme was assigned for [C$_4$mim][TOS] and [C$_4$mim][CH$_3$SO$_3$]. Analogously, three associating sites were also considered for [C$_4$mim][CF$_3$CO$_2$], one A to characterize the O$^-$ atom interactions with the cation and two B to represent the delocalized charge due to the additional oxygen and fluorine atoms.

Finally, a model with one associating site was initially proposed to describe [C$_4$mim][Br], following the same pattern attributed to [C$_n$mim][BF$_4$] [39,46], [C$_n$mim][PF$_6$] [36] and [C$_4$mim][Cl] [41] and based on the idea of an equally distributed charge. However, this model was unable to reproduce the water activity coefficients properly, as liquid–liquid immiscibility was always found when describing the mixture. In order to solve this limitation, it was decided to assign two association sites for this IL. A similar problem occurred with the [C$_4$mim][SCN] and the [C$_4$mim][CH$_3$CO$_2$], which had been fitted in a previous contribution [43] to a 1-site and a 2-site model, respectively, and were found to provide poor results for the description of water activity coefficients at 298.15 K. Hence, an additional site was added to both compounds, in order to increase the solubility of the system. More considerations about these issues are discussed in the next section. A list of the ILs modeled in this work, including the full name, molecular weight and number of associating sites of the molecular model, is provided in Table 1.

Water was modeled following a classical 4-site associating model, with 2 sites representing the two hydrogens and two sites representing the lone pair of electrons in the oxygen. The models and parameters were taken from a previous work [47]. This simple model has proven to be very successful for mixtures with some ILs [34–37].

The soft-SAFT molecular parameters of the new ILs modeled in this work (and those reformulated with additional association sites) were found by fitting to liquid density data at atmospheric pressure [48–51], as it is commonly done for ILs and polymeric systems [52], due to their negligible vapor pressures. The objective function to minimize reads:

$$F_1\left(m, \sigma, \varepsilon, \varepsilon^{HB}, \kappa^{HB}\right) = \frac{1}{N^{exp}} \sum_{i=1}^{N} \left(\frac{(\rho_{calc} - \rho_{exp})}{\rho_{exp}}\right), \tag{9}$$

being N^{exp} the total number of experimental points. As it is usual when several parameters are being regressed (in this case a total of 5), there is a certain parameter degeneracy; as a consequence, several sets provide a good description of the ILs densities. Hence, in order to minimize the impact of this degeneracy and to provide a set of robust values in all cases, one constraint was applied. Preliminary calculations showed that the volume of association, κ^{HB}, was the less sensitive parameter. Then, this parameter was assumed to be equal for all ILs and was fixed to an intermediate value of 2400 A^3, reducing Eq. (9) to four parameters. Additionally, in some particular cases, additional constraints were applied based on structural similarities. As an example, the same m value was used for the ILs [C$_4$mim][CF$_3$SO$_3$] and [C$_4$mim][CH$_3$SO$_3$], leaving the size differences of both molecules to be fully corrected by the segment diameter.

Parameter values and density modeling results are presented at Table 2 and in Fig. 1, respectively. Liquid densities for the selected ILs are described with deviations inferior to 0.30% in all cases.

Although few experimental data for these ILs are available at other conditions or for other properties, the molecular parameters found were tested, when possible, to predict the density at high pressure and/or the isothermal compressibility of these fluids, as a further test to validate them. Two examples are provided in Fig. 2 for the density at high pressure of [C$_4$mim][CF$_3$SO$_3$] [53] and the isothermal compressibility of [C$_4$mim][SCN] [54]. A slight over prediction was found for the compressibility prediction but the results were, overall, found to be satisfactory.

3.2. Vapor–liquid equilibria and water activity coefficients of IL + water systems

Once a reliable molecular model for each IL was proposed, and the correspondent molecular parameters obtained, they were applied to calculate the phase equilibria and water activity coefficients of their aqueous binary mixtures. For this purpose, isobaric VLE experimental data at 0.05, 0.07, and 0.10 MPa [29] and

Table 1
List of ionic liquids studied in this work and number of sites assigned.

Ionic liquid full name	Abbreviation	Molecular weight (g/mol)	Sites
1-butyl-3-methylimidazolium methanesulfonate	[C$_4$mim][CH$_3$SO$_3$]	234.32	3
1-butyl-3-methylimidazolium trifluoromethanesulfonate	[C$_4$mim][CF$_3$SO$_3$]	288.29	3
1-butyl-3-methylimidazolium trifluoroacetate	[C$_4$mim][CF$_3$CO$_2$]	252.23	3
1-butyl-3-methylimidazolium tosylate	[C$_4$mim][TOS]	282.36	3
1-butyl-3-methylimidazolium thiocyanate	[C$_4$mim][SCN]	197.30	2
1-butyl-3-methylimidazolium acetate	[C$_4$mim][CH$_3$CO$_2$]	198.26	3
1-butyl-3-methylimidazolium bromide	[C$_4$mim][Br]	219.12	2

Table 2
soft-SAFT molecular parameters for the selected compounds and density modeling results.

[C$_4$mim][X]	m	σ(Å)	ε/k_B(K)	ε^{HB}/k_B(K)	k^{HB}(Å^3)	%AAD
[CH$_3$SO$_3$]$^-$	4.149	4.210	360.0	4472	2400	0.103
[CF$_3$SO$_3$]$^-$	4.149	4.375	378.0	3650	2400	0.116
[CF$_3$CO$_2$]$^-$	4.180	4.256	360.7	3725	2400	0.016
[TOS]$^-$	4.896	4.389	381.0	3725	2400	0.068
[SCN]$^-$	4.295	4.076	398.0	4000	2400	0.123
[CH$_3$CO$_2$]$^-$	4.076	4.110	310.0	4837	2400	0.289
[Br]$^-$	4.496	3.885	380.0	4745	2400	0.204
Water	1.000	3.154	365.0	2388	2932	[47]

isothermal water activity coefficients data at 298.15 K [55] were used.

As a first attempt, each set of pure IL molecular parameters was used to predict the behavior of the VLE of these systems, in order to determine if quantitative agreement could be reached without fitting to binary data. However, the addition of one binary parameter was necessary in all cases to correct the deviations observed. The cross-dispersive energy parameter, ξ (see Eq. (3)), was obtained by fitting to VLE data at 0.10 MPa, minimizing the following objective function:

$$F_2(\xi) = \frac{1}{N^{exp}} \sum_{i=1}^{N} \left[\frac{(T_{calc}(P = 0.1 MPa, x) - T_{exp}(P = 0.1 MPa, x)}{T_{exp}(P = 0.1 MPa, x)} \right]$$

(10)

The fitted binary parameter, along with the molecular parameters of the IL, were used to predict the VLE of the other two isobars

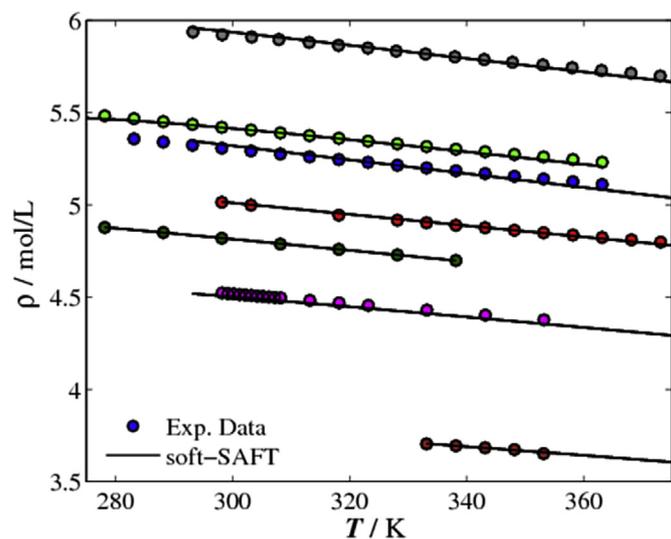**Fig. 1.** Density soft-SAFT description, from top to bottom, for [C$_4$mim][Br] (grey), [C$_4$mim][SCN] (light green), [C$_4$mim][CH$_3$CO$_2$] (blue), [C$_4$mim][CH$_3$SO$_3$] (red), [C$_4$mim][CF$_3$CO$_2$] (dark green), [C$_4$mim][CF$_3$SO$_3$] (magenta) and [C$_4$mim][TOS] (brown). Symbols are experimental data [48–51] and lines are soft-SAFT results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
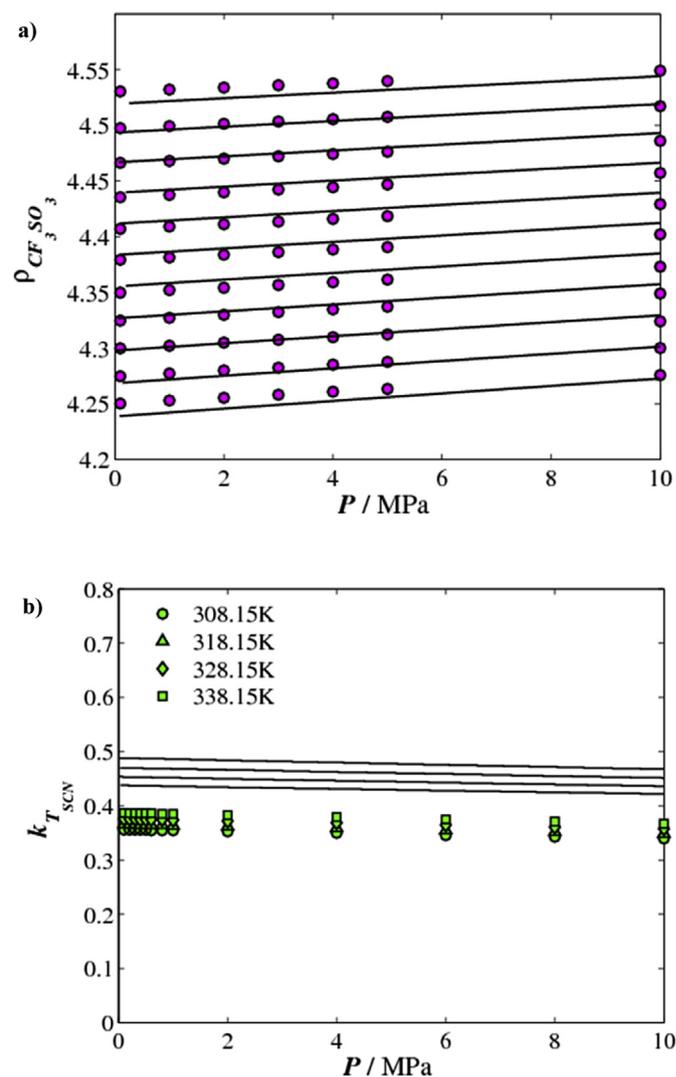

Fig. 2. a) High-pressure density prediction of [C$_4$mim][CF$_3$CO$_2$], from top to bottom, at 293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K, 343.15 K, 353.15 K, 363.15 K, 373.15 K, 383.15 K and 393.25 K. Magenta circles are experimental data [53] and full lines are the soft-SAFT predictions. b) Isothermal compressibility prediction of [C$_4$mim][SCN] at 308.15 K (circles), 318.15 K (triangles), 328.15 K (diamonds) and 338.15 K (squares). Green circles are experimental data [54] and full lines are the soft-SAFT predictions.
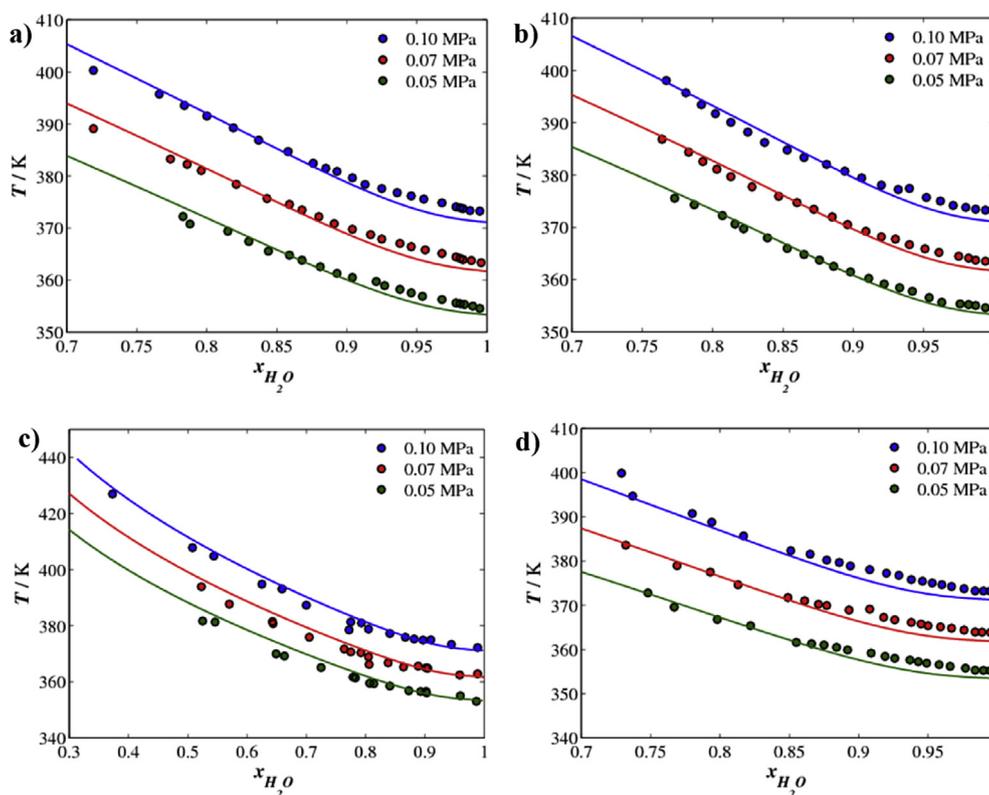
Fig. 3. Vapor–Liquid Equilibrium of selected aqueous mixtures of ILs at 0.10 MPa (blue circles), 0.07 MPa (red circles) and at 0.05 MPa (green circles) [29]. a) Water + [C₄mim][CH₃SO₃]; b) water + [C₄mim][CH₃CO₂]; c) water + [C₄mim][SCN]; d) water + [C₄mim][Br]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(0.07 MPa and 0.05 MPa), as well as the correspondent isothermal water activity coefficients at 298.15 K. The performance of the soft-SAFT EoS to describe the VLE of some of the most interesting systems is plotted in Fig. 3, while the VLE of the rest of them can be found in the Supporting Information (Figs. S1a to c). The predicted water activity coefficients for all systems are given in Fig. 4a and b. A summary of the binary parameters used for each case, as well as the average absolute deviation (AAD%) for the VLE and the water activity coefficients is provided in Table 3. In general terms, good agreement is found in all cases for the VLE (with an AAD% below 2%) and, in most of the cases, for the water activity coefficients (with an AAD% between 1.20% and 11.1%). A general observation is the fact that the binary parameter ξ, related to the cross-dispersive energy, was always fitted to values greater than one, indicating than in all cases the model underestimates the van der Waals interactions between water and the ILs.

Water with [C₄mim][CH₃SO₃] was the first studied system. The generalized combining rules for association shown in Eqs. (4) and (5) were used to compute the necessary cross-associating volume and energy between water and the ionic liquid. α^{HB} was kept equal to one. A very good representation of the VLE was achieved by fitting the ξ parameter to a value of 1.338, as it can be seen in Fig. 3a. The results are equally good for the predictions of the lower isobars. Moreover, an acceptable prediction of the water activity coefficient at 298 K is achieved (see Fig. 4a), although the soft-SAFT description slightly overpredicts the activity coefficient at high-water compositions (AAD = 8.71%). The large value of ξ reveals the strong water–anion interactions present in the nature of this mixture, generating negative deviations from ideality.

Interestingly, the substitution of the hydrogens of the anion by fluoride induces a complete change of the thermodynamic behavior of the system. This is studied in the mixture water + [C₄mim][CF₃SO₃]. Here again, a good description of the VLE is achieved at all isobars. However, this system presents positive deviations to ideality for the activity coefficient at 298 K that could not be captured using $\alpha^{HB} = 1$ (even with the use of the ξ parameter). We decided to fit α^{HB} (see Eq. (5)) using these experimental data. A lower cross-association energy was found ($\alpha^{HB} = 0.902$), indicating weak hydrogen-bonding interactions between water and the IL. With this parametrization, it was possible to find a good description of both, the VLE (Figure S1a) and the water activity coefficient (Fig. 4a), with an AAD% lower than 2.25% in both cases.

The [C₄mim][TOS] + water mixture experimental data were well described with the soft-SAFT EoS using only the ξ parameter fitted to the VLE at 0.10 MPa. Excellent predictions of the rest of the VLE diagrams (see Fig. S1b in the Supporting Information) and the water activity coefficient (Fig. 4b) were found. The increase in the water activity coefficient when compared to that of [C₄mim][CH₃SO₃] is probably due to the effect of substituting a −CH₃ in [C₄mim][CH₃SO₃] with an aromatic ring, with the correspondent decrease in the water interactions. This has been captured with soft-SAFT through an increase of the chain segment and segment diameter, m and σ, respect to the values found for [C₄mim][CH₃SO₃].

The water + [C₄mim][CH₃CO₂] was originally studied using the molecular parameters from a previous work [43] in a transferable manner. However, while the VLE was well described, a very poor prediction of the water activity coefficient at 298.15 K was obtained. Indeed, it was observed that the very strong interactions between water and this IL, translated into low water activity coefficients, required the addition of a third site to the model of [C₄mim][CH₃CO₂]. A new model was considered for this IL, and the
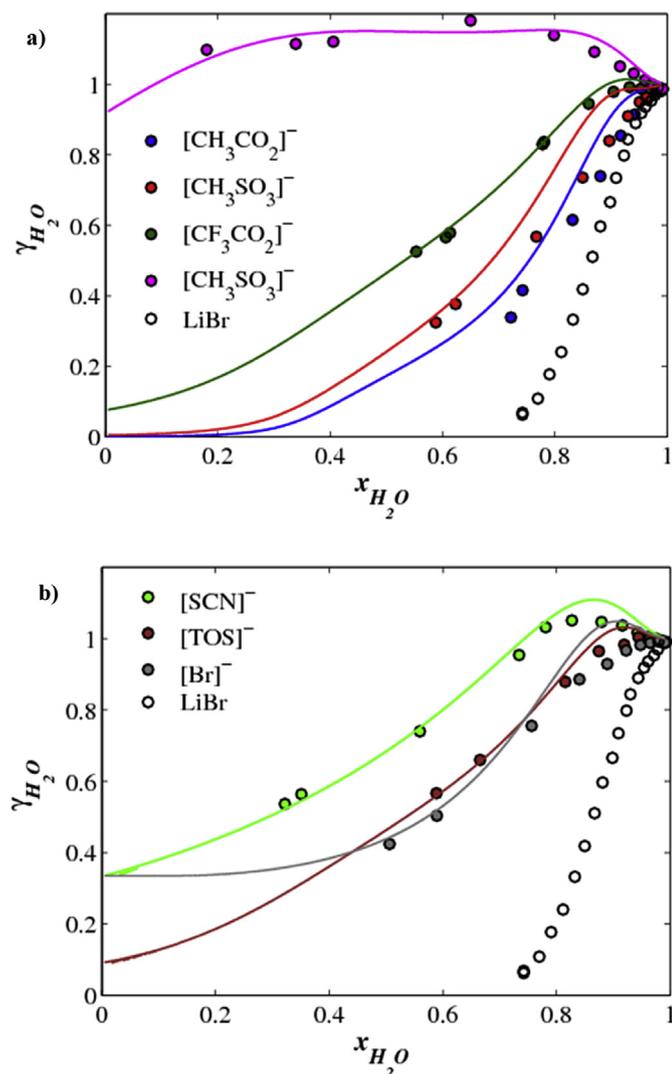
Fig. 4. Water activity coefficients at 298.15 K in a) [C$_4$mim][CH$_3$SO$_3$] (red) [C$_4$mim][CF$_3$SO$_3$] (magenta), [C$_4$mim][CF$_3$CO$_2$] (blue), [C$_4$mim][CH$_3$CO$_2$] (dark green) and LiBr (white) b) [C$_4$mim][SCN] (light green), [C$_4$mim][TOS] (brown), [C$_4$mim][Br] (grey) and LiBr (white). In both Figures, symbols are the experimental data [29,55,58], and the solid lines are soft-SAFT predictions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

parametrization with 3 sites was carried out in order to improve the results achieved. With the new model, very good agreement was obtained when compared to the VLE data for the three isobars studied (see Fig. 3b), and a good prediction of the water activity coefficient using the ξ binary parameter was also found, although the activity coefficient was slightly over predicted in the whole

Table 3
Binary parameters ξ and α^{HB} for the water + IL systems considered in this work. A value of unity means that the binary parameter was not used.

[C$_4$mim][X]	Energy Parameter	Cross-association parameter	ARD (%)	
	ξ	α^{HB} (K)	VLE	γ$_{H2O}$
[CH$_3$SO$_3$]$^-$	1.338	1.000	0.37	8.74
[CF$_3$SO$_3$]$^-$	1.177	0.902	1.73	2.22
[CF$_3$CO$_2$]$^-$	1.230	1.000	0.43	1.74
[TOS]$^-$	1.240	1.000	0.50	1.28
[SCN]$^-$	1.200	1.055	0.49	2.97
[CH$_3$CO$_2$]$^-$	1.310	1.000	1.02	11.1
[Br]$^-$	1.390	1.039	0.48	9.88

composition range (see Fig. 4b). The high hydrophilic nature of this IL, resulting from replacing the fluoride atoms by hydrogens in the anion, increased the strength of the interaction between this IL and water, showing the lowest water activity coefficients results, becoming a suitable candidate to replace classical working pairs for absorption.

A much more straightforward approach was followed for the aqueous binary mixture with [C$_4$mim][CF$_3$CO$_2$]. The VLE at all the three pressures and the water activity coefficients at 298.15 K were properly described using a value of ξ = 1.230, as depicted in Fig. S1 and Fig. 4b, respectively. The model is able to adequately describe the negative deviations from ideality typical of this system, due to the weak interactions between [C$_4$mim][CF$_3$CO$_2$] and water.

In a first trial, the description of the [C$_4$mim][SCN] was calculated using the pure compound molecular parameters optimized in a previous contribution [43], using a one-site model. Unfortunately, poor predictions of the water activity coefficient were achieved, even with the regression of a second binary parameter α^{HB} to enhance the results, as liquid−liquid (LL) immiscibility was incorrectly obtained. This is due to the fact that the original parametrization contained a very high value for the dispersive energy of [C$_4$mim][SCN] (ε^{HB}/k_B = 420.0 K). This value promotes the interaction with other ILs more than with water, giving rise to the formation of LLE. In order to overcome this limitation, a new molecular model, with two associating sites was proposed; the parameters for this model are provided in Table 2. Here, it is important to remark that, in the original contribution of Pereira and co-workers [43], a discussion about the best choice of sites for [C$_4$mim][SCN] was given based on the ability of the model to describe the solubility of CO$_2$ and N$_2$O in this IL. The conclusion was that both models (one-site and two-sites) provided equivalent results, so the choice was oriented towards the simplest one. However, when dealing with a more complex mixture such as IL + water, the one-site model seems to be limited. With the two-sites model proposed in the present work, it has been possible to lower the value of the dispersive energy (ε^{HB}/k_B = 398.0 K), as part of the energy interactions were assumed by the second association site. Now, a good description for the system is provided (Fig. 3c) using, in this case, two binary parameters: ξ for the crossed-dispersive energy and α^{HB} for the crossed-association energy. Compared to other ILs, weak interactions with water were observed at 298 K, with water activity coefficients presenting a maximum at high water concentrations. This maximum is captured with the soft-SAFT model (Fig. 4b).

The approach to model the [C$_4$mim][Br] + water system was also done in two steps. In a first attempt, a one-site model was used to describe this IL. However, the predictions of the mixture behavior did not provide a realistic picture of the phase behavior with water at 298.15 K (not shown here), the temperature at which the water activity coefficients are evaluated. Similarly to what happened for [C$_4$mim][SCN], LL immiscibility was found all the time. As a consequence, the [C$_4$mim][Br] was modeled as a chain molecule with two associating sites (see Table 2), instead of the commonly approach followed in soft-SAFT for ILs with simpler uniformly charged anions, such as [BF$_4$]$^-$ and [PF$_6$]$^-$ [36,46]. Curiously, a 2-sites model was also used to describe [C$_4$mim][Br] with PC-SAFT [29], although no details were given to justify this choice. With the new 2-sites model, a much better description of the phase behavior of the system was achieved using the ξ binary parameter (fitted to VLE at 0.10 MPa). However, an overprediction of the water coefficient on the water-rich side was still observed. In order to minimize its effect, the cross-association energy α^{HB} was adjusted achieving a final description with an AAD% of 9.88% (see Fig. 4b), while keeping an excellent description of the VLE (see Fig. 3d). Overall, soft-SAFT results are

Table 4
Infinite dilution coefficients of the systems studied in this work. Comparison between the experimental data and the soft-SAFT predicted values.

| [C$_4$mim][X] | γ_{H2O}^{∞} | | |
	Exp.data [27]	Soft-SAFT	Absolute deviation (AD)
[CH$_3$SO$_3$]$^-$	0.097	0.0054	0.092
[CF$_3$SO$_3$]$^-$	0.929	0.920	0.009
[CF$_3$CO$_2$]$^-$	0.133	0.078	0.055
[TOS]$^-$	0.167	0.092	0.075
[SCN]$^-$	0.302	0.335	0.033
[CH$_3$CO$_2$]$^-$	0.013	0.0014	0.012
[Br]$^-$	0.045	0.341	0.296

acceptable, but not as accurate as for the previous mixtures. This may be a case where the simple, yet crude model representing the cation–anion pair in the ILs as a chain molecule with associating sites mimicking the anisotropic interactions between pairs may breaks, taking also into consideration that the water model is also too crude.

For the exact representation of this system, an electrolyte term may be needed in order to incorporate the predicted complex speciation of this aqueous solution [56], also observed in other ILs + water systems [57]. In that way, it would be feasible to take into account all the formed species along the water + IL concentration range, but at the cost of an excessive increase of the soft-SAFT model complexity, specifically in the number of necessary pure compound molecular models, with the additional complexity of the cross-interactions in the mixtures. Changing the modeling approach for this mixture is out of the scope of the present work.

In Fig. 4a and b, a comparison with the water activity coefficient of a classical absorbent used in refrigeration, LiBr (empty circles) [54], is plotted. Although not as hydrophilic as LiBr, [C$_4$mim][CH$_3$SO$_3$] and [C$_4$mim][CH$_3$CO$_2$] show interactions close to that of LiBr, being potential replacements as alternative absorbents without the shortcomings of this common salt.

Finally, the infinite dilution coefficients of the systems studied in this work were also calculated from soft-SAFT using Eq. (7) (reduced to Eq. (8)), as presented in Table 4. A comparison between the experimental data and the soft-SAFT predicted values is also presented, indicating the absolute deviations ($AD = \left| \gamma_{H2O}^{\infty,SAFT} - \gamma_{H2O}^{\infty,exp} \right|$) in all cases. As it can be seen, predictions are quite good in all cases, except for the water + [C$_4$mim][Br] system, for the reasons previously discussed.

4. Conclusions

In this work, the phase equilibria at three different pressures and the water activity coefficients at 298.15 K of 7 binary aqueous mixtures of [C$_4$mim] ILs with different anions were described with the soft-SAFT EoS. The particular systems were chosen as potential candidates to be possible pairs of absorption cooling systems.

Different coarse-grained models based on different association schemes within the soft-SAFT approach were proposed for the ionic liquids [C$_4$mim][CH$_3$SO$_3$], [C$_4$mim][CF$_3$SO$_3$], [C$_4$mim][CF$_3$CO$_2$], [C$_4$mim][TOS] and [C$_4$mim][Br]. The [C$_4$mim][CH$_3$CO$_2$] and [C$_4$mim][SCN] molecular models were also revised for a better description of the mixture thermodynamic behavior. Each binary system was then individually studied regarding deviations from ideality. An appropriate cross-association scheme was also proposed to describe the short-range association forces between water and the ionic liquids. One or, in some cases, two binary parameters, related to the energy of the systems, were used to achieve a simultaneous description of the VLE and water activity coefficients.

The simple model used in soft-SAFT, where ILs are represented as chain molecules with associating sites, provided an overall good description of most of the systems, with an AAD% lower than 2% for the VLE calculations and an AAD% between 1.20 and 11.1% for the water activity coefficients. Results of some particular systems point towards some improvements in the soft-SAFT model of ILs (and water) to better take into account the species formed when mixed with water or other highly polar fluids. At the expense of adding complexity to the model, the description of these systems may be slightly improved.

Nevertheless, the presented soft-SAFT modeling development already stands as a valuable tool to describe the VLE and water activity coefficients in binary aqueous mixtures of [C$_4$mim] ILs with different anions, having a robust methodology that can be expendable to other aqueous IL binary systems, and to additional properties, in order to provide key information on the design and implementation of new absorption cooling systems.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2016.02.017.

Nomenclature

Symbols

A	Helmholtz energy
g_{LJ}	Radial distribution function of a fluid of LJ spheres
k_B	Boltzmann's constant
κ^{HB}	Association site volume
m	Number of segments
F	Objective function
N	Number of points
P	Pressure
T	Temperature
x_i	Molar fraction of the component i
α^{HB}	Binary parameter for correcting deviation from the cross-association energy
ε/k_B	Dispersive energy between segments forming the chain
ε^{HB}/k_B	Association site energy
ρ	Density
Σ	Segment diameter
ξ	Binary parameter for correcting deviations in the dispersive energy
φ	Fugacity coefficient
γ	Activity coefficient

Superscripts

assoc	Association interactions term
chain	Chain term
exp	Experimental
HB	Hydrogen bonding

L	Liquid Phase
ref	Reference term
sat	Saturation
∞	Infinite

Subscripts

B	Boltzmann
i	Component i
j	Component j
o	Initial

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