



Evaluation of the solvent structural effect upon the vapor–liquid equilibrium of $[C_4C_1im][Cl]$ + alcohols



Naima Chouireb^{a,b}, Imran Khan^c, Emanuel A. Crespo^b, Mariana B. Oliveira^b,
Fèlix Llovell^d, Lourdes F. Vega^e, O. Tafat-Igoudjilene^a, A. Ait Kaci^a, Luís M.N.B.F. Santos^f,
Pedro J. Carvalho^{b,*}, João A.P. Coutinho^b

^a Laboratory of Thermodynamic and Molecular Modeling, Faculty of Chemistry, USTHB, BP 32, El-Alia, Bab-Ezzouar, Algies, Algeria

^b CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^c Department of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, PC 123, Muscat, Oman

^d IQS School of Engineering, Department of Chemical Engineering and Materials Science, Universitat Ramon Llull, Via Augusta, 390, 08017 Barcelona, Spain

^e Gas Research Center and Chemical Engineering Department, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arabs Emirates

^f Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, P-4169-007 Porto, Portugal

ARTICLE INFO

Article history:

Received 19 December 2016

Received in revised form

23 February 2017

Accepted 24 February 2017

Available online 27 February 2017

Keywords:

Vapor-liquid equilibrium

1-Butyl-3-methylimidazolium chloride

Alcohols

Isomers

Soft –SAFT

Activity coefficients

Binary mixtures

Alkyl chain length

ABSTRACT

A systematic isobaric vapor-liquid equilibrium (VLE) study of seven binary mixtures of 1-butyl-3-methylimidazolium chloride, $[C_4C_1im][Cl]$, and methanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, tert-butanol (2-methylpropan-2-ol), iso-butanol (2-methylpropan-1-ol) and pentan-1-ol, was carried out at three different system pressures (0.1, 0.07 and 0.05 MPa). Activity coefficients were estimated from the boiling temperatures of the binary mixtures. soft-SAFT equation of state was used to describe the experimental VLE data and all together, allowed to infer and understand the effect of the alcohol alkyl chain length and structural isomerism on the molecular interactions between the IL and the alcohols.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Vapor-liquid equilibrium (VLE) data for azeotropic or close-boiling systems are crucial for better understanding the thermodynamic behavior and design of separation processes [1]. The separation of azeotropic mixtures has conventionally been one of the most challenging tasks in industrial processes since simple distillation stood unfeasible. Several other separation processes suitable for azeotrope mixtures separation, like extractive distillation, pressure swing distillation, liquid-liquid extraction and adsorption membranes, have been developed. Among them, extractive distillation is the most widely used for azeotrope

separation. Based on the addition of a third solvent with a high boiling point, *i.e.* entrainer, the system relative volatility is modified promoting the separation [1]. Organic solvents [2], inorganic salts [3], hyper-branched polymers [4] or dendrimers [5] have been investigated as feasible entrainers. Recently, ionic liquids (ILs), a novel class of solvents, have attracted an increased interest as entrainers for extractive distillation [1–6].

The use of ILs can stand as a technologically and environmentally favorable alternative to traditional entrainers in separation of organic substances. ILs have received a continuous attention in the past years as solvents with enhanced potential and feasible solvents to replace volatile organic solvents, mainly due to their exceptional physical and chemical properties. They are organic salts whose organic cation and inorganic or organic anion asymmetry and/or charge dispersion allows them to remain liquid at temperatures below 373 K. The cation and the anion can be selected and

* Corresponding author.

E-mail address: quijorge@ua.pt (P.J. Carvalho).

tuned to design an IL with a set of desired properties. By interchanging cations and anions about 10^6 pure ILs can be synthesized [7,8]. The possibility of tuning the IL properties, targeting a specific application and/or interaction, arose the interest in using ILs as environmentally friendly entrainers for the separation of azeotropic mixtures.

Despite its undeniable interest, most of the works available focus on the interaction of ILs with water and less on the interaction of ILs with alcohols, in particular on the analysis of the effect of the alcohol structure upon the interactions with ILs [9–31]. In this work, isobaric VLE of a series of alcohols, namely methanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, iso-butanol, tert-butanol and pentan-1-ol, with the 1-butyl-3-methylimidazolium chloride ($[C_4C_1im][Cl]$) was evaluated aiming at understanding both the effect of alkyl chain length and the structural isomerism, of the alcohols, on the interactions and, consequently, on the VLE.

The nature and strength of the interactions established between the alcohol and the IL can be evaluated based on the non-ideality of the mixture [32,33]. Several thermodynamic methods have been used for correlating experimental phase equilibrium data of ILs-containing systems [34–36]. Among them, Statistical Associating Fluid Theory (SAFT), on its several variants, have been used due to their capability to describe the association type interactions at a molecular level [37–41]. Soft-SAFT has been successfully applied to the description of system with alcohols [40,42] and ionic liquids [43–47] and thus was here used to describe the phase equilibrium of the studied mixtures.

2. Experimental section and modeling

2.1. Materials

Methanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol (iso-butanol), 2-methylpropan-2-ol (tert-butanol), pentan-1-ol and 1-butyl-3-methylimidazolium chloride, $[C_4C_1mim][Cl]$, was acquired from IoLiTec (Germany) with a mass fraction purity higher than 99%. In order to reduce to negligible values both water and volatile compounds, vacuum (10^{-3} mbar), stirring and moderate temperature (303 K) were applied prior to the measurements for a period of at least 48 h. Furthermore, during the experimental procedure the IL, used to prepare new mixtures, was kept under vacuum. The compounds systematical name, chemical structures, suppliers, purities, purification method and final water mass fractions are summarized in Table 1.

2.2. Vapor-liquid equilibrium

The VLE of the binary systems under study was determined at (0.1, 0.07 and 0.05) MPa using an isobaric microbullometer developed and optimized in our group; the equipment description can be found in detail in previous publications [48,49]. The temperature of the liquid phase was measured with a fast response glass-sealed Pt100 class 1/10 probe, with a standard uncertainty of 0.05 K and a temperature resolution of 0.002 K. The temperature probe was calibrated prior to the measurements by comparison with a NIST-certified Fluke calibration 1521 thermometer, with an uncertainty of 5×10^{-3} K. The internal system pressure was monitored and kept constant through a Büchi vacuum pump (model V-700) and a Büchi pressure controller unit (model V-850). The pressure was measured using a MKS Baratron type capacitance Manometer (model 728A) kept at 100 °C (to avoid condensation),

with an accuracy of 0.5% and uncertainty of 0.5 mbar. The equilibrium was assumed when the temperature was constant (temperature drift lower than ± 0.05 K/min) for at least 5 min. The liquid phase composition was determined through an Anton Paar Abbe-mat 500 Refractometer, with an uncertainty of 2×10^{-5} nD, using a calibration curve, previously established, and able to allow the determination of the sample composition within ± 0.001 mol fraction. The adequacy of the apparatus and methodology adopted to measure this type of systems was previously established [48,49].

2.3. Soft-SAFT EoS

The general expression for SAFT type equations is given in terms of the residual Helmholtz free energy, typically expressed as the sum of three terms: a reference term (A^{ref}), defined as the contribution to the Helmholtz energy of the fluid due to the monomer-monomer interactions; a chain term (A^{chain}), that considers chain formation; and an association term (A^{assoc}), which explicitly takes into account short-range attractive interactions, such as hydrogen bonding [37,50]. Additional terms, such as polar contributions, can be added depending on the compounds under consideration.

$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} \quad (1)$$

All SAFT-type equations use the chain and association term developed by Wertheim [51–53], differing in the reference term. A Lennard-Jones (LJ) spherical fluid is used as a reference potential in soft-SAFT, taking into account the repulsive and attractive interactions of the monomers constituting the chain, being described by means of the Johnson's et al. equation [54].

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 energy and volume of association, ϵ_{ij}^{HB}/k_B and κ_{ij}^{HB} , respectively.

To extend soft-SAFT to mixtures, the van der Waals one-fluid theory with the generalized Lorentz-Berthelot (LB) combining rules for the size, σ_{ij} , and energy, ϵ_{ij} , parameters are applied:

$$\sigma_{ij} = \eta_{ij} \left(\frac{\sigma_{ii} + \sigma_{jj}}{2} \right) \quad (2)$$

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

being η_{ij} the size and ξ_{ij} the energy binary parameters, accounting for size and energy asymmetries, respectively. These values become one when using a predictive approach and are typically regressed from binary experimental data. ξ_{ij} is equivalent to $(1-k_{ij})$ in most EoS. The cross-association values of the volume (κ_{ij}^{HB}) and energy (ϵ_{ij}^{HB}/k_B) parameters to account for the volume and energy of association between different compounds are also needed. These values are obtained from pure component parameters using the following combining rules:

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

$$\epsilon_{ij}^{HB} = (\epsilon_{ii}^{HB} \epsilon_{jj}^{HB})^{1/2} \quad (5)$$

Molecular model. A key element for the accurate prediction of the phase equilibrium and thermophysical properties from molecular-based EoSs is the selection of a reliable coarse-grained model that can represent the basic physical features of the

Table 1
Systematical name, chemical structures, suppliers, purification method, purities and final water mass fractions.

Name	Supplier	Purification method	Purity ^a	Water content $w_{H_2O}\%$ ^b	Chemical structure
Methanol	Sigma Aldrich	Molecular sieves	0.990	0.0054	
Propan-1-ol	Lab-Scan	Molecular sieves	0.995	0.0057	
Propan-2-ol	Sigma Aldrich	Molecular sieves	0.998	0.0048	
Butan-1-ol	Panreac	Molecular sieves	0.995	0.0500	
Butan-2-ol	Prolabo	Molecular sieves	0.990	0.0200	
2-methylpropan-1-ol (iso-butanol)	Sigma Aldrich	Molecular sieves	0.990	0.0500	
2-methylpropan-2-ol (tert-butanol)	Sigma Aldrich	Molecular sieves	0.993	0.0600	
Pentan-1-ol	Alfa Aesar	Molecular sieves	0.990	0.0120	
1-butyl-3-methylimidazolium chloride [C ₄ C ₁ im][Cl]	IoLiTec	Drying Procedure	0.990	0.0001	

^a ¹H, ¹³C NMR.

^b Karl Fischer titration.

compounds to be modeled.

Methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol were previously considered as homo-nuclear chainlike molecules of equal diameter, σ , and the same dispersive energy, ϵ . Alkanols' hydroxyl group is described by two square-well sites embedded off-centre in one of the LJ segments [55,56]. In this work, these compounds molecular parameters were taken from the literature [55,56]. For the remaining alcohols the same molecular model was selected and molecular parameters were regressed from vapor pressure and liquid density data taken from the DIPPR database [57]. It should be taking into account that soft-SAFT, as all versions of SAFT, is based on Wertheim's first order perturbation theory [51–53]. As a consequence, the equation is unable to distinguish the location of the pending groups, and hence, there is not an explicit differentiation between isomers. The differences in the isomers are considered in an effective manner, by the specific values of the molecular parameters, which somehow take into account the differences in molecular volume and energy of the isomers.

Mac Dowell et al. [58] have considered [C₄C₁im][Cl] with only one association site to represent the IL–IL interactions. The molecular parameters for this ionic liquid used in this work were selected from the publication of Mac Dowell and coworkers [58].

All parameters and modeling results for the properties used on their regression, when carried out in this work, are presented at Table 2.

3. Results and discussion

Experimental isobaric VLE data for binary systems of [C₄C₁im][Cl] with the selected alcohols were measured at (0.1, 0.07 and 0.05) MPa, ionic liquid mole fractions up to 0.6 and temperatures up to 430 K, as depicted in Figs. 1 and 2 and reported in Tables S1 through

S8 (in supporting information). The phase diagram for the binary mixture of [C₄C₁im][Cl] and ethanol has been retrieved from our previous publication [48]. To the best of our knowledge no VLE data for the studied systems were previously available in the literature.

The capability of soft-SAFT to successfully describe the phase equilibria of ionic liquid systems was here confirmed by the description of the experimental VLE data. Using no more than one, pressure independent, binary interaction parameter to express the deviations of the cross-association energies from the combining rules used (Eqs. (4) and (5)), the model was able to provide a good description of the phase equilibria of the different systems studied with an %AAD of 2.5%. Energy binary parameters greater than one were necessary for all the systems considered in order to overcome the model underestimation of the dispersive interactions between the species. The parameters used to describe the systems here

Table 2

Soft-SAFT molecular parameters and modeling results for the compounds evaluated in this work.

Compound	m_i	$\sigma_{ii}/\text{\AA}$	$\epsilon_{ii}/k_B/K$	$\epsilon^{HB}_{ii}/k_B/K$	$\kappa_{ii}^{HB}/\text{\AA}^3$	%AAD	
						p^g	ρ
methanol	1.491 ^a	3.375 ^a	220.4 ^a	3213 ^a	4847 ^a		
ethanol	1.740 ^a	3.635 ^a	234.8 ^a	3387 ^a	2641 ^a		
Propan-1-ol	1.971 ^a	3.808 ^a	252.7 ^a	3450 ^a	2250 ^a		
Butan-1-ol	2.210 ^a	3.940 ^a	269.2 ^a	3450 ^a	2250 ^a		
Pentan-1-ol	2.420 ^a	4.051 ^a	283.7 ^a	3450 ^a	2250 ^a		
Propan-2-ol	1.942	3.820	226.4	3450	2250	0.17	0.023
Butan-2-ol	2.352	3.821	231.9	3450	2250	0.93	0.90
tert-butanol	2.103	3.969	215.8	3450	2250	0.23	0.023
iso-butanol	2.156	3.968	256.3	3450	2250	0.88	0.11
[C ₄ C ₁ im][Cl]	4.650 ^b	3.795 ^b	454.2 ^b	2200 ^b	2250 ^b		

^a Ref: [56].

^b Ref: [58].

studied are presented at Table 3 and the modeling results depicted at Figs. 1 and 2.

3.1. The binary systems non-ideality

The non-ideality of the binary systems can be evaluated in terms of the activity coefficient of component i (γ_i), using the modified Raoult's law

$$\gamma_i = \frac{y_i \phi_i}{x_i \phi_i^s p_i^s} \quad (6)$$

where p and p_i^s are the system pressure and the saturation pressure, at the system temperature. y_i and x_i represent the vapor and liquid phase mole fractions, respectively. The ϕ_i is the fugacity coefficient in the vapor phase and ϕ_i^s the fugacity coefficient in its saturated state. At the pressures investigated in this study the fugacity coefficients are close to unity. Furthermore, due to the IL low volatility the system vapor phase is composed entirely by the alcohol, allowing Eq. (6) to be simplified as,

$$\gamma_i = \frac{p}{x_i p_i^s} \quad (7)$$

The saturation pressure of the alcohols were estimated using correlations obtained from DIPPR's database [57].

The calculated activity coefficients for the studied systems, at 0.1 MPa, are depicted in Fig. 3 and reported in supporting information.

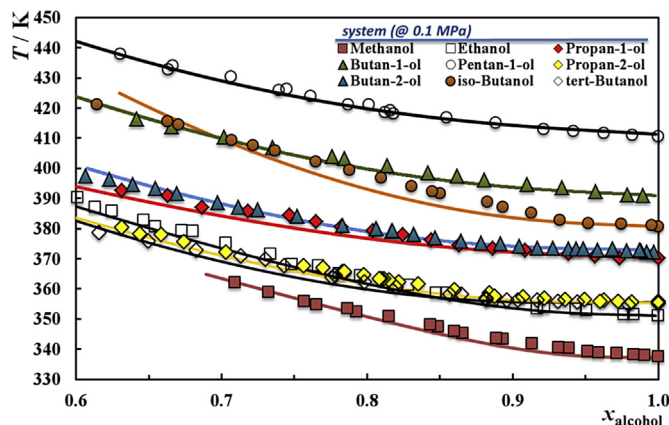


Fig. 2. Isobaric temperature-composition diagram of the binary systems [C₄C₁im][Cl] + alcohol at 0.1 MPa. The binary system [C₄C₁im][Cl] + ethanol was taken from our previous work [48]. The solid lines represent the soft-SAFT EoS description of the experimental data.

As shown in Fig. 3, most of the IL solutions in alcohols present activity coefficients close to one in the region of high IL dilution (until mole fractions around 90%). This is an indication that in the regime of full solvation of the ionic liquid pair the cohesive interaction of alcohols with this IL is quite similar to that of the alcohol – alcohol. On the other hand in the more hindered hydroxyl group type alcohols as tert-butanol, butan-2-ol and even propan-2-ol, the

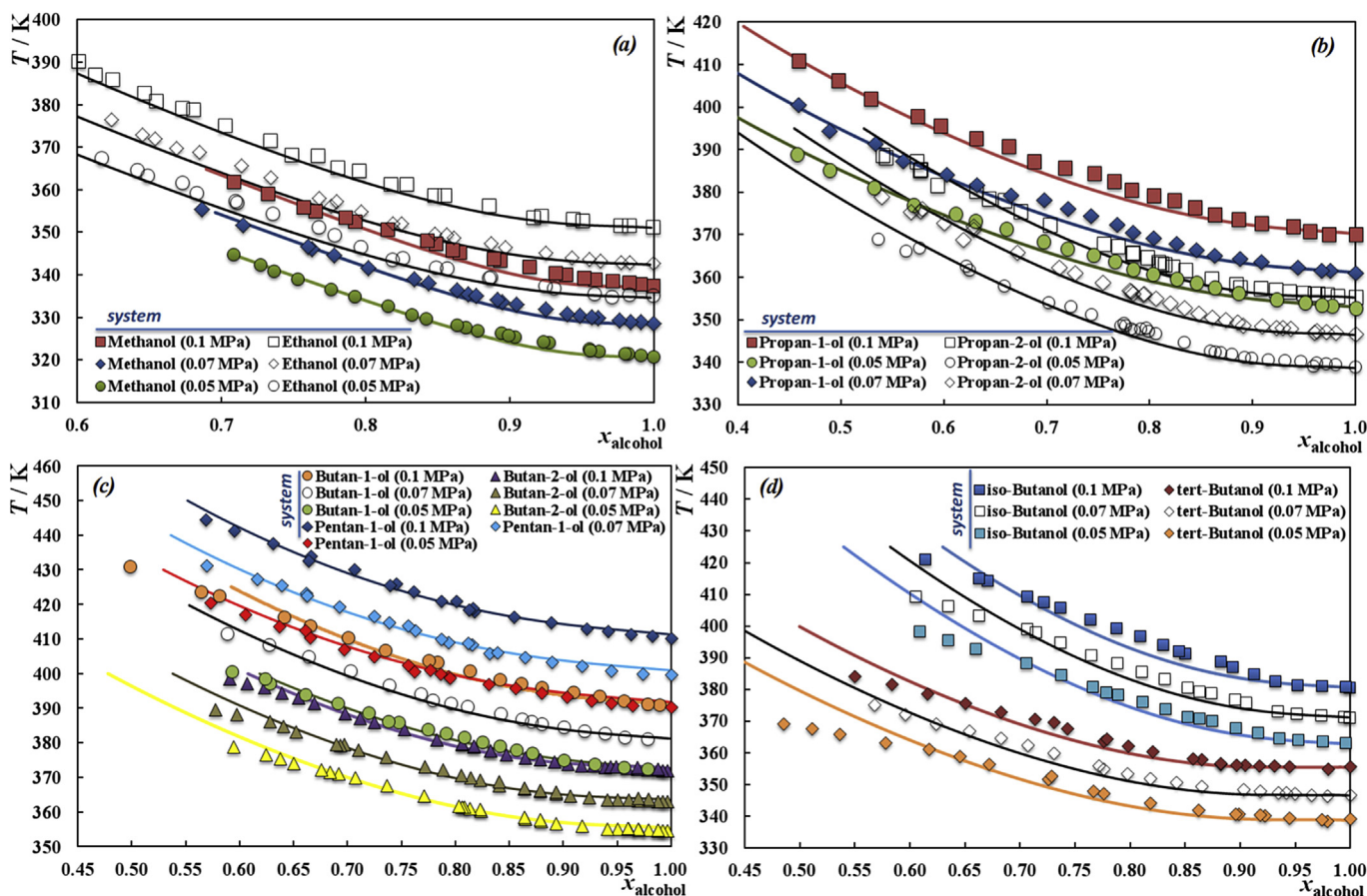


Fig. 1. Isobaric temperature-composition diagram of the binary systems [C₄C₁im][Cl] + alcohol at 0.1, 0.07 and 0.05 MPa. The binary system [C₄C₁im][Cl] + ethanol was taken from our previous work [48]. The solid lines represent the soft-SAFT EoS description of the experimental data.

Table 3
Soft-SAFT binary parameters for the Alcohol + IL systems evaluated in this work.

[C ₄ C ₁ im][Cl] +	Energy binary parameter ξ	[C ₄ C ₁ im][Cl] +	Energy binary parameter ξ	[C ₄ C ₁ im][Cl] +	Energy binary parameter ξ
methanol	1.32	Butan-1-ol	1.24	Butan-2-ol	1.28
ethanol	1.30	Pentan-1-ol	1.21	tert-butanol	1.35
Propan-1-ol	1.21	Propan-2-ol	1.30	iso-butanol	1.38

activity coefficients are greater than one in dilute IL solutions highlighting the decrease of the hindered hydroxyl group interaction with the IL compared with the alcohol – alcohol. For the mixtures with higher molar concentration of IL (mole fraction of alcohol lower than 90%) a regular decrease of the activity coefficient was found for all alcohols indicating a favorable intermolecular interaction between the species. Although the activity coefficient decrease with the more hindered hydroxyl group alcohols, it is systematically lower than those of the more less hindered hydroxyl group alcohols (terminal groups), which indicates less favorable intermolecular interaction between the species.

The soft-SAFT equation was also used to describe the alcohol activity coefficients as presented in Fig. 3. Overall, soft-SAFT is able to describe very well the systems' activity coefficients even though some over-estimation of the activity coefficients is observed for a couple of systems. Similarly to a previous work [47], where the VLE and water activity coefficients were described for water + IL systems, improvements could be achieved by regressing a cross-association energy binary parameter to the experimental data. Nevertheless the soft-SAFT descriptions can be considered acceptable, showing a very good activity coefficient versus alcohol composition dependency description, (%AAD of 5.1%) using only one pressure independent binary interaction parameter and the common combining rules for the cross-association volume and energy, with no expense of adding complexity and losing the predictive character of the model.

3.2. Effect of the alcohols' alkyl chain length and structural isomerism upon the VLE

An assessment of the effect of alcohols on the boiling temperatures and activity coefficients of the studied VLE systems at 0.1 MPa, is depicted in Figs. 3 and 4. As shown, both on the linear as on the branched alcohols the increase of the alkyl chain length leads to an increase of the boiling temperature of the system. This result, combined to the fact that all the alcohols studied have just one hydroxyl group, suggests that the increase of the boiling temperature is due to the increase of the van der Waals dispersion forces. Thus, increasing the alkyl chain length increases the ability of individual molecules to interact with each other that, in turn, increases the boiling temperature. The activity coefficients, on the other hand, denote a far more complex behavior, with the increase of the alkyl chain length, from methyl to propyl, leading to an increase of the activity coefficients, denoting weaker intermolecular interactions as a result of a charge delocalization on the hydroxyl group (decrease of the hydrogen bond capability) as well as, to the decrease of the relative height of the hydroxyl group interaction among the total alcohol cohesive interaction. Nonetheless, the butan-1-ol presents similar activity coefficients than those of the propan-1-ol and pentan-1-ol. This behavior suggests that, for alkyl chain lengths longer than propyl, the alkyl chain increase imposes no further impact on the hydroxyl group charge delocalization and thus, on the hydrogen bond strength, while leading to increasing van der Waals dispersion forces interactions. In fact this is taken into account in the soft-SAFT model, where the association parameters are kept constant and independent of the chain length for

alcohols with three or more carbons. In addition, the lower dependence of the activity coefficients with the alkyl chain length (after propan-1-ol) is an indication that the hydroxyl group is involved in the major interaction between alcohols and the IL.

Within structural isomers, the hydroxyl group position at other than a terminal position, lowers the mixtures boiling temperatures. Moreover, increasing the alcohol branching leads to a decrease of the boiling temperatures. This is due to the fact that branching leads to an increase of the hydroxyl group hindrance as well as a decrease on the interaction surface area and consequently a decrease of van der Waals interactions, as depicted in Figs. 5 and 6. Therefore, the intermolecular attractive forces (van der Waals), which depend upon the surface area, become weaker in magnitude on account of the branching. Moreover, the surface area decrease leads to higher surface charge delocalization, hindering the intermolecular interactions leading thus, to lower boiling temperatures. Similar to that observed for the linear alcohols, the alkyl chain length increase and the addition of methyl groups, in the alkyl chain, leads to enhanced intermolecular dispersion interactions.

Overall, the hydrogen-bond capability, even though present, seems to play a less relevant role with the increase of the hydrocarbon moiety, as depicted in Fig. 6 by the H-Bond (H_{HB}) and van der Waals (H_{vdW}) interaction energies, taken from COSMO-RS (C30-1401) at 298.15 K.

Moreover, the boiling temperature increase with the alcohol alkyl chain increase is consistent with the results of mutual solubility reported in the literature [59,60].

4. Conclusions

A systematic isobaric vapor-liquid equilibrium study of eight binary mixtures of 1-butyl-3-methylimidazolium chloride with methanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, tert-butanol (2-methylpropan-2-ol), iso-butanol (2-methylpropan-1-ol) and pentan-1-ol, is here reported for the first time for alcohol mole fractions down to 0.4 and at three different system pressures (0.1, 0.07 and 0.05 MPa). The alkyl chain length increase, both on the linear as on the branched alcohols, leads to an increase of the system boiling temperature.

Within structural isomers, the hydroxyl group position at other than a terminal position, make the alcohols "less aliphatic" leading thus to lower boiling temperatures. Moreover, branching makes the molecule more compact, with smaller surface area and therefore, weaker dispersion forces that lead to lower boiling temperatures. Furthermore, even though hydrogen-bond capability is still present it seems to play a less relevant role and is very well reflected in the differentiation that was observed in the behavior of the outlier alcohols as methanol and ethanol as well as in the more crowded and hindered hydroxyl group as the tert-butanol, butan-2-ol and even propan-2-ol.

The Soft-SAFT capability to describe the phase equilibria of the studied systems was shown. New molecular parameters, for four alcohols, were regressed from vapor pressure and liquid density and using just one pressure independent binary interaction parameter the model was able to describe very well the phase equilibria and the alcohols activity coefficients of the various

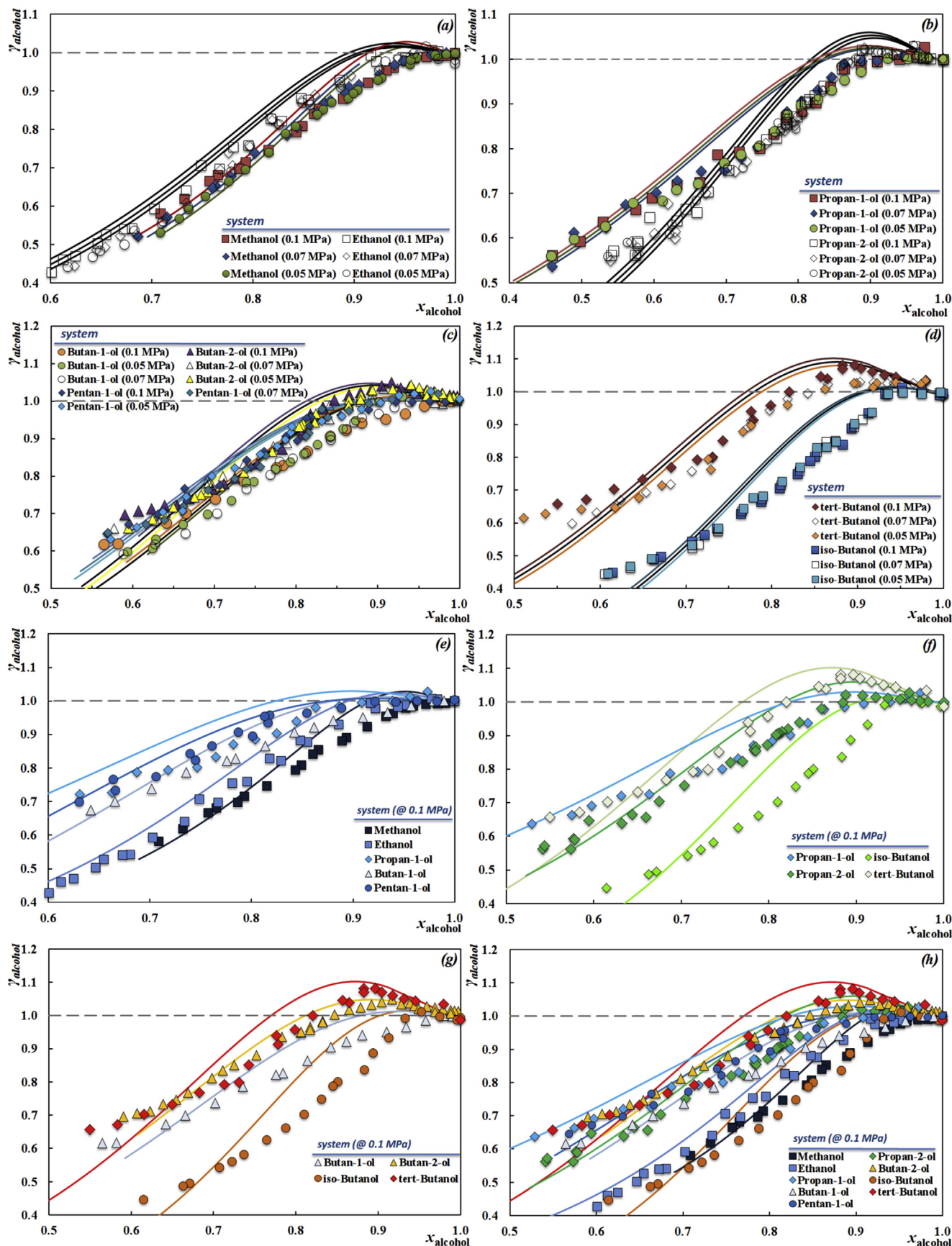


Fig. 3. Activity coefficients as function of the alcohol mole fraction of the binary systems $[C_4C_{1m}][Cl]$ + alcohol at 0.1, 0.07 and 0.05 MPa. The binary system $[C_4C_{1m}][Cl]$ + ethanol was taken from our previous work [48]. The solid lines represent the soft-SAFT EoS fit to the experimental data.

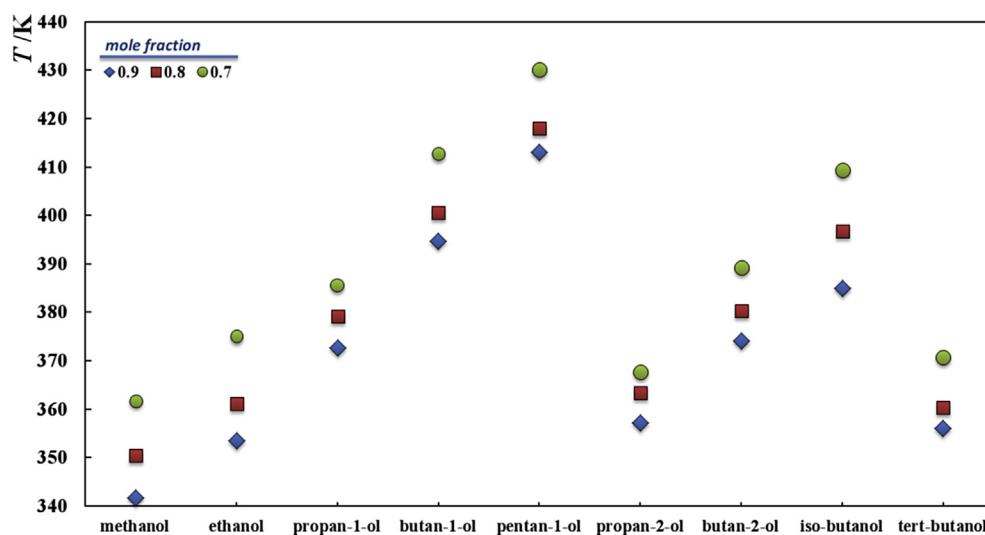


Fig. 4. Boiling points as function of the alcohol and its concentration, at 0.1 MPa.

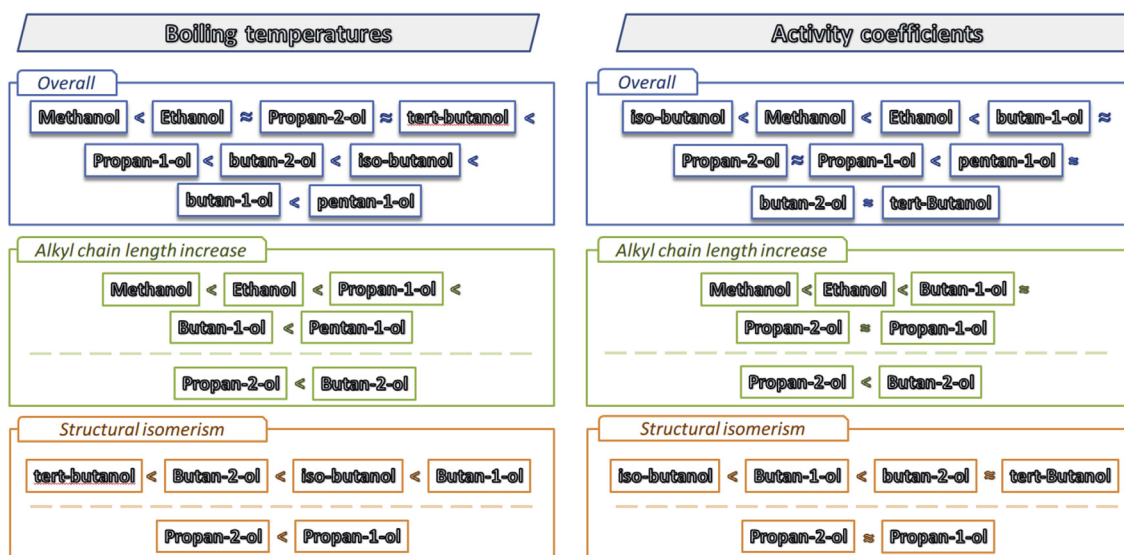


Fig. 5. Boiling temperature and activity coefficient trends at 75% alcohol mole fraction.

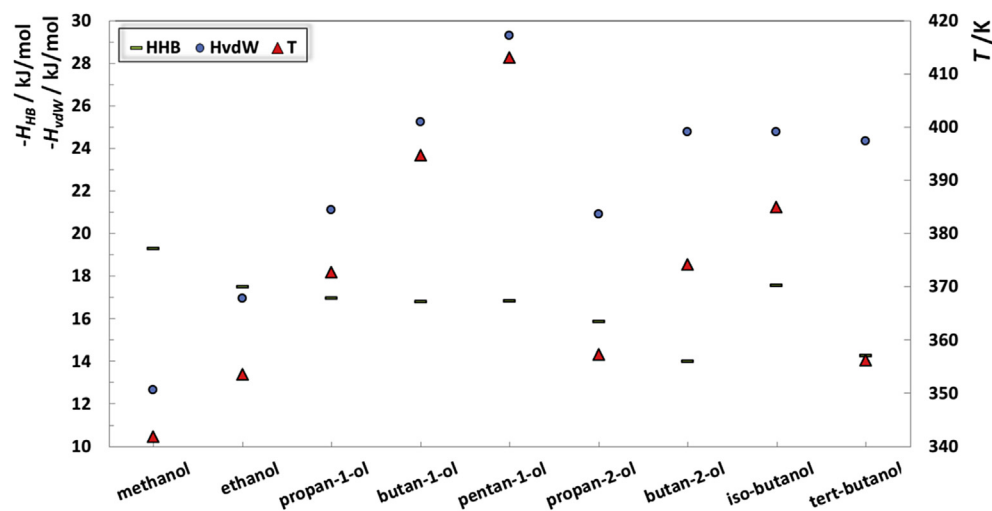


Fig. 6. Hydrogen-bond (H_{HB}) and van der Waals (H_{vdW}) interaction energy, at 298.15 K, and boiling temperature of the alcohol + IL binary systems at 0.9 alcohol mole fraction.

systems studied.

Acknowledgements

This work was developed in the scope of the project CICECO – Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (Ref. FCT UID/CTM/50011/2013) and CIQUP-University of Porto (Projects: PEst-C/QUI/UI0081/2013, FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065), financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. On the Spanish side, financial support was provided by AGAUR, from the Catalan Government (2014SGR-1582). The authors acknowledge FCT for the exploratory project grant (EXPL/QEQ-PRS/0224/2013). I. Khan and M.B. Oliveira acknowledge FCT for the postdoctoral grants SFRH/BPD/76850/2011 and SFRH/BPD/71200/2010, respectively. P.J. Carvalho acknowledges FCT for a contract under the Investigador FCT 2015, contract number IF/00758/2015.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.fluid.2017.02.016>.

References

- [1] A.B. Pereiro, J.M.M. Araújo, J.M.S.S. Esperança, I.M. Marrucho, L.P.N. Rebelo, Ionic liquids in separations of azeotropic systems – a review, *J. Chem. Thermodyn.* 46 (2012) 2–28.
- [2] I. Blume, J.G. Wijmans, R.W. Baker, The separation of dissolved organics from water by pervaporation, *J. Memb. Sci.* 49 (1990) 253–286.
- [3] T. Zhigang, Z. Rongqi, D. Zhanting, Separation of isopropanol from aqueous solution by salting-out extraction, *J. Chem. Technol. Biotechnol.* 76 (2001) 757–763.
- [4] M. Seiler, C. Jork, A. Kavarnou, W. Arlt, R. Hirsch, Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids, *AIChE J.* 50 (2004) 2439–2454.
- [5] K. Inoue, Functional dendrimers, hyperbranched and star polymers, *Prog. Polym. Sci.* 25 (2000) 453–571.
- [6] W. Li, D. Sun, T. Zhang, S. Dai, F. Pan, Z. Zhang, Separation of acetone and methanol azeotropic system using ionic liquid as entrainer, *Fluid Phase Equilib.* 383 (2014) 182–187.
- [7] J.D. Holbrey, K.R. Seddon, Ionic liquids, *Clean. Technol. Environ. Policy* 1 (1999) 223–236.
- [8] A. Hult, M. Johansson, E. Malmström, Hyperbranched polymers, in: *Adv. Polym. Sci.* 1999, pp. 1–34.
- [9] N. Yaghini, L. Nordstierna, A. Martinelli, Effect of water on the transport properties of protic and aprotic imidazolium ionic liquids – an analysis of self-diffusivity, conductivity, and proton exchange mechanism, *Phys. Chem. Chem. Phys.* 16 (2014) 9266.
- [10] S. Cha, M. Ao, W. Sung, B. Moon, B. Ahlström, P. Johansson, Y. Ouchi, D. Kim, Structures of ionic liquid–water mixtures investigated by IR and NMR spectroscopy, *Phys. Chem. Chem. Phys.* 16 (2014) 9591–9601.
- [11] P. D'Angelo, A. Zitolo, G. Aquilanti, V. Migliorati, Using a combined theoretical and experimental approach to understand the structure and dynamics of imidazolium-based ionic liquids/water mixtures. 2. EXAFS spectroscopy, *J. Phys. Chem. B* 117 (2013) 12516–12524.
- [12] M. López-Pastor, M.J. Ayora-Cañada, M. Valcárcel, B. Lendl, Association of methanol and water in ionic liquids elucidated by infrared spectroscopy using two-dimensional correlation and multivariate curve resolution, *J. Phys. Chem. B* 110 (2006) 10896–10902.
- [13] B. Hribar, N.T. Southall, V. Vlachy, K. a Dill, How ions affect the structure of water how ions affect the structure of water, *J. Am. Chem. Soc.* 124 (2002) 12302–12311.
- [14] M. Klahn, C. Stuber, A. Seduraman, P. Wu, What determines the miscibility of ionic liquids with Water? Identification of the underlying factors to enable a straightforward prediction, *J. Phys. Chem. B* 114 (2010) 2856–2868.
- [15] Y. Kohno, H. Ohno, Ionic liquid/water mixtures: from hostility to conciliation, *Chem. Commun.* 48 (2012) 7119–7130.
- [16] T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, The association of water in ionic liquids: a reliable measure of polarity, *Angew. Chem. Int. Ed.* 45 (2006) 3697–3702.
- [17] C.G. Hanke, R.M. Lynden-Bell, A simulation study of Water–Dialkylimidazolium ionic liquid mixtures, *J. Phys. Chem. B* 107 (2003) 10873–10878.
- [18] L. Zhang, Z. Xu, Y. Wang, H. Li, Prediction of the solvation and structural properties of ionic liquids in water by two-dimensional correlation spectroscopy, *J. Phys. Chem. B* 112 (2008) 6411–6419.
- [19] L.E. Ficke, J.F. Brennecke, Interactions of ionic liquids and water, *J. Phys. Chem. B* 114 (2010) 10496–10501.
- [20] N. Calvar, B. Gonzalez, E. Gómez, A. Domínguez, Vapor–Liquid equilibria for the ternary system ethanol + water + 1-Butyl-3-methylimidazolium methylsulfate and the corresponding binary systems at 101.3 kPa, *J. Chem. Eng. Data* 54 (2009) 1004–1008.
- [21] N. Calvar, B. González, E. Gómez, Á. Domínguez, Vapor–Liquid equilibria for the ternary system ethanol + water + 1-Butyl-3-methylimidazolium chloride and the corresponding binary systems at 101.3 kPa, *J. Chem. Eng. Data* 51 (2006) 2178–2181.
- [22] N. Calvar, B. González, E. Gómez, A. Domínguez, Study of the behaviour of the azeotropic mixture ethanol–water with imidazolium-based ionic liquids, *Fluid Phase Equilib.* 259 (2007) 51–56.
- [23] N. Calvar, E. Gómez, B. Gonzalez, A. Domínguez, Experimental Vapor–Liquid equilibria for the ternary system ethanol + water + 1-Ethyl-3-methylpyridinium Ethylsulfate and the corresponding binary systems at 101.3 kPa: study of the effect of the cation, *J. Chem. Eng. Data* 55 (2010) 2786–2791.
- [24] A.V. Orchill, P.J. Miguel, F.J. Llopis, E. Vercher, A.V. Orchillés, A. Martínez-Andreu, Isobaric vapor–liquid equilibria for the extractive distillation of ethanol + water mixtures using 1-Ethyl-3-methylimidazolium dicyanamide, *J. Chem. Eng. Data* 56 (2011) 4875–4880.
- [25] L. Zhang, J. Han, R. Wang, X. Qiu, J. Ji, Isobaric Vapor–Liquid equilibria for three ternary systems: water + 2-propanol + 1-Ethyl-3-methylimidazolium tetrafluoroborate, water + 1-propanol + 1-Ethyl-3-methylimidazolium tetrafluoroborate, and water + 1-propanol + 1-Butyl-3-methylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 52 (2007) 1401–1407.
- [26] Q. Li, F. Xing, Z. Lei, B. Wang, Q. Chang, Isobaric vapor–liquid equilibrium for isopropanol + water + 1-Ethyl-3-methylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 53 (2007) 275–279.
- [27] A. Westerholt, V. Liebert, J. Gmehling, Influence of ionic liquids on the separation factor of three standard separation problems, *Fluid Phase Equilib.* 280 (2009) 56–60.
- [28] Q. Li, J. Zhang, Z. Lei, J. Zhu, B. Wang, X. Huang, Isobaric vapor–liquid equilibrium for (Propan-2-ol + water + 1-Butyl-3-methylimidazolium tetrafluoroborate), *J. Chem. Eng. Data* 54 (2009) 2785–2788.
- [29] L.-Z. Zhang, D.-S. Deng, J.-Z. Han, D.-X. Ji, J.-B. Ji, Isobaric Vapor–Liquid equilibria for water + 2-propanol + 1-Butyl-3-methylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 52 (2007) 199–205.
- [30] M. Döker, J. Gmehling, Measurement and prediction of vapor–liquid equilibria of ternary systems containing ionic liquids, *Fluid Phase Equilib.* 227 (2005) 255–266.
- [31] L. Zhang, Y. Ge, D. Deng, J. Ji, Effect of ionic liquids on (vapor + liquid) equilibrium behavior of (water + 2-methyl-2-propanol), *J. Chem. Thermodyn.* 41 (2009) 138–143.
- [32] J.P. Gutiérrez, G.W. Meindersma, A.B. De Haan, COSMO-RS-based ionic-liquid selection for extractive distillation processes, *Ind. Eng. Chem. Res.* 51 (2012) 11518–11529.
- [33] Z. Lei, C. Dai, J. Zhu, B. Chen, Extractive distillation with ionic liquids: a review, *AIChE J.* 60 (2014) 3312–3329.
- [34] M.G. Freire, S.P.M. Ventura, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, Evaluation of COSMO-RS for the prediction of LLE and VLE of water and ionic liquids binary systems, *Fluid Phase Equilib.* 268 (2008) 74–84.
- [35] I. Rodríguez-Palmeiro, O. Rodríguez, A. Soto, C. Held, Measurement and PC-SAFT modelling of three-phase behaviour, *Phys. Chem. Chem. Phys.* 17 (2015) 1800–1810.
- [36] H. Passos, I. Khan, F. Mutelet, M.B. Oliveira, P.J. Carvalho, L.M.N.B.F. Santos, C. Held, G. Sadowski, M.G. Freire, J.A.P. Coutinho, Vapor–liquid equilibria of water + alkyimidazolium-based ionic liquids: measurements and perturbed-chain statistical associating fluid theory modeling, *Ind. Eng. Chem. Res.* 53 (2014) 3737–3748.
- [37] F.J. Blas, L.F. Vega, Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory, *Mol. Phys.* 92 (1997) 135–150.
- [38] L.F. Vega, F. Llovel, F.J. Blas, Capturing the solubility minima of n-Alkanes in water by Soft-SAFT, *J. Phys. Chem. B* 113 (2009) 7621–7630.
- [39] F.R. Varanda, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho, Liquid–liquid equilibrium of substituted perfluoro-n-octane+n-octane systems, *Fluid Phase Equilib.* 268 (2008) 85–89.
- [40] F. Llovel, L.F. Vega, Global fluid phase equilibria and critical phenomena of selected mixtures using the crossover soft-SAFT equation, *J. Phys. Chem. B* 110 (2006) 1350–1362.
- [41] L.F. Vega, F. Llovel, Review and new insights into the application of molecular-based equations of state to water and aqueous solutions, *Fluid Phase Equilib.* 416 (2016) 150–173.
- [42] F. Castro-Marcano, C.G. Olivera-Fuentes, C.M. Colina, Joule-Thomson inversion curves and third virial coefficients for pure fluids from molecular-based models, *Ind. Eng. Chem. Res.* 47 (2008) 8894–8905.
- [43] L.F. Vega, O. Vilaseca, F. Llovel, J.S. Andreu, Modeling ionic liquids and the solubility of gases in them: recent advances and perspectives, *Fluid Phase Equilib.* 294 (2010) 15–30.
- [44] F. Llovel, E. Valente, O. Vilaseca, L.F. Vega, Modeling complex associating mixtures with [Cn-mim][T2N] ionic liquids: predictions from the soft-SAFT equation, *J. Phys. Chem. B* 115 (2011) 4387–4398.

- [45] J.S. Andreu, L.F. Vega, Capturing the solubility behavior of CO₂ in ionic liquids by a simple model, *J. Phys. Chem. C* 111 (2007) 16028–16034.
- [46] J.S. Andreu, L.F. Vega, Modeling the solubility behavior of CO₂, H₂, and Xe in [Cn-mim][Tf₂N] ionic liquids, *J. Phys. Chem. B* 112 (2008) 15398–15406.
- [47] M.B. Oliveira, E.A. Crespo, F. Llovel, L.F. Vega, J.A.P. Coutinho, Modeling the vapor-liquid equilibria and water activity coefficients of alternative refrigerant-absorbent ionic liquid-water pairs for absorption systems, *Fluid Phase Equilib.* 426 (2016) 100–109.
- [48] P.J. Carvalho, I. Khan, A. Morais, J.F.O. Granjo, N.M.C. Oliveira, L.M.N.B.F. Santos, J.A.P. Coutinho, A new microbulliometer for the measurement of the vapor-liquid equilibrium of ionic liquid systems, *Fluid Phase Equilib.* 354 (2013) 156–165.
- [49] I. Khan, M.L.S. Batista, P.J. Carvalho, L.M.N.B.F. Santos, J.R.B. Gomes, J.A.P. Coutinho, Vapor-liquid equilibria of imidazolium ionic liquids with cyano containing anions with water and ethanol, *J. Phys. Chem. B* 119 (2015) 10287–10303.
- [50] F.J. Blas, L.F. Vega, Prediction of binary and ternary diagrams using the statistical associating fluid theory (SAFT) equation of state, *Ind. Eng. Chem. Res.* 37 (1998) 660–674.
- [51] M.S. Wertheim, Fluids with highly directional attractive forces. I. Statistical thermodynamics, *J. Stat. Phys.* 35 (1984) 19–34.
- [52] M.S. Wertheim, Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations, *J. Stat. Phys.* 35 (1984) 35–47.
- [53] M.S. Wertheim, N. Brunswick, Fluids with highly directional attractive forces. IV. Equilibrium polymerization, *J. Stat. Phys.* 42 (1986) 477–492.
- [54] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, The Lennard-Jones equation of state revisited, *Mol. Phys.* 78 (1993) 591–618.
- [55] F. Llovel, O. Vilaseca, N. Jung, L.F. Vega, Water+1-alkanol systems: modeling the phase, interface and viscosity properties, *Fluid Phase Equilib.* 360 (2013) 367–378.
- [56] J.C. Pàmies, *Bulk and Interfacial Properties of Chain Fluids*, Universitat Rovira i Virgili, 2003.
- [57] DIPPR database v10.0 Brigham Young University, Design Institute for physical properties, DIPPR DIADEM Database DIADEM Predict. Softw. (1998).
- [58] N. Mac Dowell, F. Llovel, N. Sun, J.P. Hallett, A. George, P.A. Hunt, T. Welton, B.A. Simmons, L.F. Vega, New experimental density data and soft-SAFT models of alkylimidazolium ([CnC1im]⁺) chloride (Cl⁻), methylsulfate ([MeSO₄]⁻), and dimethylphosphate ([Me₂PO₄]⁻) based ionic liquids, *J. Phys. Chem. B* 118 (2014) 6206–6221.
- [59] J.M. Crosthwaite, M.J. Muldoon, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, Liquid phase behavior of ionic liquids with alcohols: experimental studies and modeling, *J. Phys. Chem. B* 110 (2006) 9354–9361.
- [60] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, Liquid phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions, *Fluid Phase Equilib.* 228–229 (2005) 303–309.