



Assessing the N₂O/CO₂ high pressure separation using ionic liquids with the soft-SAFT EoS



Luís M.C. Pereira^a, Mariana B. Oliveira^a, Felix Llovel^b,
Lourdes F. Vega^{b,c}, João A.P. Coutinho^{a,*}

^a CICECO, Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

^b MATGAS Research Center, Campus de la UAB, 08193 Bellaterra, Barcelona, Spain

^c Carbueros Metálicos/Air Products Group, C/Aragón 300, 08009 Barcelona, Spain

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ABSTRACT

The capabilities of the soft-SAFT EoS to accurately describe the thermophysical properties of ionic liquids (ILs) and the phase equilibria of their mixtures with greenhouse gases is extended in this work to address the CO₂ and the N₂O solubilities in [C₄mim]⁺ ILs from different anion families. In addition to the commonly studied [BF₄]⁻ and [NTf₂]⁻ anions, the solubility of these gases in ILs with the anions [N(CN)₂]⁻, [SCN]⁻ and [Ac]⁻ is also studied and compared among them, searching for the best system for separation purposes.

A coarse-grained molecular model is proposed within the soft-SAFT framework for each newly studied IL based on structural information, guidance obtained from quantum calculations and previous work. The most adequate set of molecular parameters are selected from the ILs density description and from the ability to reproduce the N₂O/CO₂ solubilities in these ILs at the lowest and highest temperatures for which experimental data are available. A discussion about the association molecular parameters values and their relation with the anion nature is also presented.

With these molecular models, the description of the high pressure phase equilibria of the binary systems composed of the two gases and the ILs referred above are described with soft-SAFT for the remaining isotherms. For most systems, the equilibria behavior of the mixtures is predicted without using any binary parameter. When good agreement with the experimental data is not achieved, a single temperature independent binary parameter is enough to allow a good description. Finally, Henry's law constants are calculated from soft-SAFT to evaluate the selectivity of those ILs for the CO₂/N₂O separation.

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1. Introduction

Ionic liquids (ILs) have been the focus of large research attention in different areas of application, due to their remarkable and tunable characteristics. One of them is their use as solvent replacements of those typically employed in the traditional greenhouse gases capture processes [1]. ILs are known to have an extremely low vapor pressure, negligible flammability, high thermal and chemical stability, highly solvating capacity and low corrosivity. These characteristics can provide process enhancements on this field [2–5].

Looking at the available literature it is possible to see that carbon dioxide (CO₂) is the most commonly studied compound when investigating the use of ionic liquids in pollutant gases separation and capture processes. This preference for CO₂ is understandable

by the amount of research devoted in recent years to find more efficient materials for CO₂ capture and separation [6]. A closer look reveals that [NTf₂]⁻ ILs are the most studied [7–12], as a result of [NTf₂]⁻ being established by IUPAC as a benchmark anion in ILs for extensive investigation [13].

Nevertheless, nitrous oxide (N₂O), produced both from natural and industrial sources, is also considered a potent greenhouse gas, with considerable atmospheric lifetime and global warming potential (GWP = 300) [14]. It also has a major contribution to the ozone layer depletion [15], while it also finds some interesting industrial applications, such as a reagent for selective oxidations [16]. With this scenario, the use of ILs as a medium for N₂O separation and capture processes is seen as a promising alternative.

As happens with any new or already existing process, the design and/or operation optimization of separation processes for these gases using ILs requires the capability to accurately describe greenhouse gases solubility in ILs in large ranges of compositions, temperatures and pressures. For this reason, an adequate

* Corresponding author. Tel.: +351 234401507; fax: +351 234370084.

E-mail address: jcoutinho@ua.pt (J.A.P. Coutinho).

thermodynamic model is necessary, overcoming the costs and, often, the difficulties of the experimental measurements of this kind.

The common cubic equations of state (EoS) derived from the van der Waals theory are the most frequently used for describing the high pressure phase equilibria of gas + ionic liquids systems. Considering the N_2O + ILs mixtures, much less studied than the CO_2 systems, the Peng–Robinson and the Redlich–Kwong EoS are the predominant choices for the phase equilibria description, as it happens for the CO_2 solubility in ILs [17]. A Redlich–Kwong based EoS with up to four binary interaction parameters was developed by Shiflett et al. [18,19] for the correlation of the N_2O solubility in six ionic liquids, [bmim][Tf₂N], [bmim][BF₄], [bmim][N(CN)₂], [bmim][Ac], [eam][NO₃] and [bmim][SCN], while Revelli et al. [20] applied the simplified PPR78 model with temperature dependent binary interaction parameters to describe the N_2O solubility in five ionic liquids, [bmim][BF₄], [bmim][SCN], [dmim][MP], [(ETO)₂IM][Tf₂N] and [(OH)₂IM][Tf₂N].

Although good results were obtained with these approaches, they are limited on their transferability and predictive abilities, as seen by the overall necessity to use a considerable number of binary interaction parameters, some of them temperature dependent, regressed from experimental data. These results show the need to refine the theoretical basis of EoS, explicitly considering the different physical features of the pure components and their mixtures.

Molecular based models, such as the Statistical Associating Fluid Theory (SAFT), are an alternative in this case. One of the SAFT versions, which has shown accurate descriptions of the phase equilibria of gas + ILs systems, is the soft-SAFT EoS [21–28]. In 2007, Andreu and Vega were able to reproduce the solubility of CO_2 in several ILs of the families [C_nmim][BF₄] and [C_nmim][PF₆] using a quite simple, but yet accurate model [21]. A year later, the same authors described the solubility of H₂ and Xe in ILs of the [C_nmim][Tf₂N] family [22]. The model for the [C_nmim][BF₄] was also later applied to the description of the BF₃ solubility in [C₄mim][BF₄] in reference [23], while the molecular parameters of the [C_nmim][Tf₂N] family were refined and extended to model mixtures with alcohols and water in a subsequent publication [24]. In 2011 and 2012, Lovell et al. [25,26] described the solubility of NH₃, SO₂, H₂S, CO₂ and H₂ in ILs from the families [C_nmim][BF₄], [C_nmim][PF₆] and [C_nmim][Tf₂N]. The solubilities of CO₂ and SO₂ in ionic liquids of the [C_nmpy][NTf₂] family were also addressed in [27], while the CO₂, N₂O, CH₄ and the N₂ solubilities in [C₂mim][CH₃OHPO₂] were reported recently [28]. It is worthy to remark the excellent results obtained in these studies when using the soft-SAFT equation with relatively simple molecular models.

One of the main features of soft-SAFT, mostly responsible for the good results obtained on the description of the solubility of gases in ILs, is the statistical mechanics basis of the approach. The equation explicitly considers intermolecular interactions among the molecules, providing physical meaning and molecular parameters independent of the thermodynamic conditions. Before applying the equation, a physical interpretation for each compound is made and an adequate molecular model is proposed, specifically accounting for molecular shape and multiple dispersive, hydrogen-bonding and polar interactions among the molecules [29]. These coarse-grained models within the soft-SAFT context were also considered on the ILs studies previously mentioned, explicitly considering the key features of the complex nature of the cation–anion pair and their anisotropic interactions, while keeping the model as simple as possible.

In this work, the application of the soft-SAFT EoS to the description of gas + ionic liquid systems is further investigated. CO_2 , and the much less studied N_2O , solubilities in 1-butyl-3-methylimidazolium based ILs with different anions are addressed, adding new anions families not previously fully considered

in SAFT approaches. The ionic liquids here studied are the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf₂N], the 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄], the 1-butyl-3-methylimidazolium dicyanamide [bmim][N(CN)₂], the 1-butyl-3-methylimidazolium thiocyanate [bmim][SCN] and the 1-butyl-3-methylimidazolium acetate [bmim][Ac].

To our knowledge, only Chen et al. [30] have modeled the imidazolium ionic liquids with the anions [SCN][−], [Ac][−] and [N(CN)₂][−] with a SAFT approach (PC-SAFT). However, their study considered only the estimation of the pure compound parameters of these ILs for the density description. Although the description of the CO_2 solubility was evaluated for the ILs with the anions [BF₄][−], [PF₆][−], [Tf₂N][−] and [CF₃SO₃][−], CO_2 systems with the ILs formed by the above mentioned anions were not considered.

Since these ILs are modeled for the first time with soft-SAFT, association schemes need to be proposed for each of them, and the best molecular parameters values must be established. For each one, coarse-grained molecular models are proposed guided by the conductor-like screening model for realistic solvation tool (COSMO-RS) quantum calculations software [31] and the previously gathered experience with ILs. CO_2/N_2O solubility predictions and the anion polarity representation are also presented. Finally, the soft-SAFT EoS is used to compute CO_2 and N_2O Henry's law constants for the evaluation of the selectivity of each IL, in order to determine which one has the best CO_2/N_2O gas separation performance.

2. Results and discussion

The soft-SAFT EoS [32,33] is one of the most successful modifications of the original SAFT proposed by Chapman et al. [34] and Huang and Radosz [35]. As the other SAFT versions, its chain and associating terms are based on Wertheim's first-order thermodynamic perturbation theory (TPT1), while for the reference term it specifically uses a Lennard–Jones (LJ) spherical fluid, which takes into account the repulsive and the attractive interactions of the monomers that constitute the chain. The soft-SAFT EoS expressions and details can be found elsewhere [21–28,32,33] and will be not repeated here.

Before applying a molecular association EoS like soft-SAFT to the description of the phase equilibria of gas + IL systems, the selection of a reliable coarse-grained model that represents the basic physical features of the compounds, including the main physical short-range interactions, is an essential first step.

The molecular model and set of parameters for CO_2 and N_2O were taken from previous works [28,36] (Table 1). CO_2 and N_2O were modeled as non-associating but polar compounds, composed by a homonuclear LJ chain in which explicit quadrupolar interactions are considered by means of an effective quadrupole moment, Q_i , contained in a certain fraction of the molecule ($x_{pi} = 1/3$). The value of x_{pi} mimics the CO_2 and N_2O molecule resonance structure with three segments with a quadrupole in one of them.

The [BF₄][−] and [NTf₂][−] ILs had also been previously addressed by soft-SAFT. Alkyl-imidazolium ionic liquids with the [BF₄][−] anion were considered to be homonuclear chainlike molecules with one associating site in each molecule, describing the specific cation–anion interactions due to the charges and the asymmetry [21]. Alkyl-imidazolium ionic liquids with the [NTf₂][−] anion were modeled with three associating sites representing the cation–anion interactions; one A type associating site represents the nitrogen atom interactions with the cation, and two B sites represent the delocalized charge due to the oxygen molecules on the anion, allowing only AB interactions between different ionic liquid molecules [24]. The molecular parameters values for [C₄mim][BF₄]

Table 1
Soft-SAFT EoS molecular parameters for the compounds studied in this work.

	m_i	σ_{ii} (Å)	ε_{ii}/k_B (K)	$\varepsilon_{ii}^{HB}/k_B$ (K)	K_{ii}^{HB} (Å ³)	Q_i (C m ²)	ρ (%AAD)	P^σ (%AAD)	Number associating sites	Reference
CO ₂	1.571	3.184	160.20			4.4×10^{-40}	0.90	0.50		Dias et al. [36]
N ₂ O	1.391	3.360	175.58			5.0×10^{-40}	1.54	3.27		Pereira et al. [28]
[C ₄ mim][BF ₄]	4.495	4.029	420.00	3450	2250		<0.2		1	Andreu et al. [21]
[C ₄ mim][NTf ₂]	6.175	4.211	399.41	3450	2250		0.09		3	Llovel et al. [24]
[C ₄ mim][N(CN) ₂]	5.700	3.754	384.28	3850	2450		0.19		2	This work
[C ₄ mim][SCN]	4.966	3.879	420.00	3850	2850		0.10		1	This work
[C ₄ mim][Ac]	5.872	3.699	397.45	4450	3950		0.037		2	This work

and [C₄mim][NTf₂] are taken from these previous publications [21,24] and are included in Table 1 for completeness.

Similar molecular models were investigated and proposed in this work for the other three ionic liquids from different anions families, dicyanamide ([N(CN)₂]⁻), thiocyanate ([SCN]⁻) and acetate ([Ac]⁻), for which no soft-SAFT model was, up to now, proposed. COSMO-RS calculations were used to generate surface charge density representations and σ -profile $p(\sigma)$ graphs. COSMO-RS is a theory based on quantum calculations, which describes the interactions in a fluid as local contact interactions of molecular surfaces. Those interaction energies are quantified by the values of the two screening charge densities σ and σ' , which form a molecular contact. In COSMO-RS, the charge density is measured as the response of an electric conductor to the charge density of the molecule and, therefore, it gives the relative amount of surface with polarity on the surface of a molecule. An approximate pattern between the number of peaks and association points to be considered is then suggested, from which a coarse grained model of the molecules can be inferred. However, it is important to remark that COSMO-RS is not used as an approach that provides a unique answer about the number of association sites, but as a tool to assess a reasonable choice from a physical perspective, taking also into account additional information about the structure and behavior of the systems.

Molecular parameters were regressed from ionic liquids atmospheric pressure liquid density data, finding several sets that provide a very good description of these data. The problems associated with parameter degeneracy in SAFT-type approaches are well recognized and they become more severe when modeling ionic liquids, as vapor pressure is not included in the fitting. In this work, we have chosen the best set of molecular parameters values based on their ability to predict the solubility data of CO₂ and N₂O.

2.1. CO₂ and N₂O solubilities in [C₄mim][BF₄] and [C₄mim][NTf₂]

In previous publications [21,22], soft-SAFT EoS was used to compute the CO₂ solubility in [C₄mim][BF₄] and in [C₄mim][NTf₂], using one binary interaction parameter, which was temperature independent and very close to unity ($\xi = 0.985$ for [C₄mim][BF₄] and $\xi = 0.972$ for [C₄mim][NTf₂]). As the behavior of CO₂ + [C₄mim][BF₄]/[C₄mim][NTf₂] mixtures at high pressures was successfully reproduced with soft-SAFT by Andreu and Vega [21,22], this is not addressed here again.

In this work, the N₂O high pressure solubility in these two ionic liquids is addressed for the first time with soft-SAFT. Experimental data available from Shiflett et al. [19,37] at four different temperatures, ranging from 283.14 K to 347.86 K, are used for comparison. In a first attempt, the binary parameter ξ was transferred from the one used for CO₂ mentioned in the previous paragraph. Although reasonable agreement was achieved in both cases with this highly predictive approach, we decided to improve these results by fitting the binary parameter ξ to the intermediate temperatures of these systems. In agreement with these

results, the binary interaction parameter was considered temperature independent and the same value of 0.980 was used for both [C₄mim][NTf₂] and [C₄mim][BF₄] systems at all isotherms. Using this transferable approach for the binary interaction parameters for the N₂O + [C₄mim][NTf₂]/[C₄mim][BF₄] mixtures, quantitative agreement between the experimental data and the model results was obtained, as observed in Fig. 1a and b, respectively.

One of the advantages of using this type of equations is the ability to predict the behavior at other ranges of temperature, pressure or composition where data are not available. Being confident with our model, in good agreement with the experimental data at low N₂O compositions, a vapor–liquid–liquid (VLE) region for both [C₄mim][NTf₂] and [C₇mim][BF₄] systems is predicted at high N₂O compositions, with a lower critical solution temperature (LCST) at about 267 K and 253 K, respectively, and the temperature of the critical endpoint at 333 K and 330 K, respectively. The appearance of liquid–liquid immiscibility at high gas concentrations is in agreement with the experimental data at 282.7 K and 293.6 K presented by Shiflett et al. [19,37] for the N₂O + [C₄mim][NTf₂] system (see Fig. 1a), while our predictions describe a slightly smaller VLE region for the N₂O + [C₄mim][BF₄] mixture (see Fig. 1b).

It is important to mention that, although no numerical issues have been encountered, particular care in the initial guesses has been taken in order to avoid falling onto unphysical roots of the equation at low temperatures, as it is known to occur in several SAFT-type formulations for systems composed of a small and a relatively big molecule [38]. For this case and the rest of the series, a top-down approach, starting the calculations close to the critical end point and decreasing the temperature, has been successfully used.

2.2. [C₄mim][N(CN)₂]: molecular model and CO₂ and N₂O solubilities

[C₄mim][N(CN)₂] is assessed for the first time with soft-SAFT in this work. As explained before, in order to propose an appropriate molecular model for this ionic liquid, COSMO-RS calculations were used as a guide, generating anions σ -profile $p(\sigma)$ graphs and surface charge density representations.

The [N(CN)₂]⁻ σ -profile ($p(\sigma)$) presents one peak around 1.5 e/Å² and another close to 0.5 e/Å² – hence, less charged – (Fig. 2), attributed to the anion N⁻ atom and to the delocalized charge due to the two additional N⁻ atoms present in the anion. This guided us to consider the [C₄mim][N(CN)₂] ionic liquid as an associating molecule with two sites, one A site representing the N⁻ atom interactions with the cation, while one B site represents the delocalized charge due to the two extra N⁻ atoms on the anion. A sketch of the model is also presented in Fig. 2.

Comparison with the work of Chen et al. [30] with PC-SAFT reveals that these authors considered one association site to describe [C₄mim][N(CN)₂] based on, as reported, the studies of Llovel et al. [24] and Andreu and Vega [21] when addressing the [C₇mim][Tf₂N], [C₇mim][BF₄] and the [C₇mim][PF₆] ILs families. No

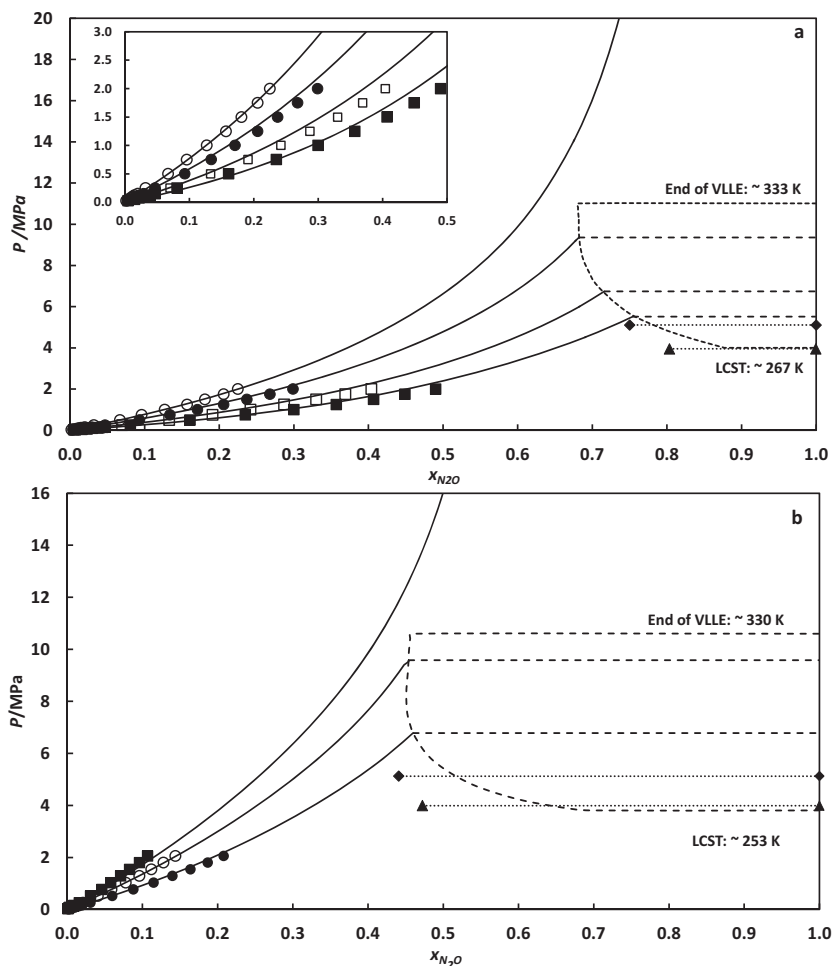


Fig. 1. Pressure-composition diagram of the binary systems. (a) $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{NTf}_2]$ (VLE: \blacksquare , 283.14 K; \square , 298.10 K; \bullet , 323.12 K; \circ , 347.6 K; and VLLE: \blacktriangle , 282.7 K; \blacklozenge , 293.6 K) and (b) $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{BF}_4]$ (VLE: \bullet , 298.10 K; \circ , 323.14 K; \square , 347.94 K, and VLLE: \blacktriangle , 282.7 K; \blacklozenge , 293.6 K). Symbols are experimental data [19,37] and the solid and the dashed lines represent the soft-SAFT EoS results for the VLE and the VLLE, respectively.

further explanation is presented for the choice of one association site.

Once the association model was selected, molecular parameters were regressed using liquid density data at atmospheric pressure [39]. Several sets of molecular parameters providing a good liquid density description were obtained with the minimization of the relative least-squares objective function. To differentiate among them and select the most appropriate ones, their ability to predict the high pressure phase equilibria data of the systems

$\text{CO}_2/\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ was tested. Further assessment was done by comparing the parameters values obtained with other values from previously studied ionic liquids composed of other anions, particularly the association parameters. High pressure experimental data for the systems $\text{CO}_2/\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ were available from Carvalho et al. [40] and Shiflett et al. [19] at four different temperatures, from 283.13 K to 363.19 K.

The best sets of parameters are provided in Table S1 from the Supporting Information, along with the deviations obtained

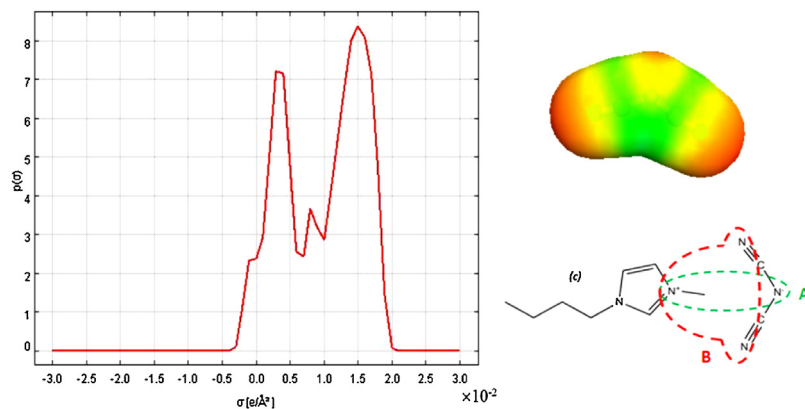


Fig. 2. $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ σ -profile $p(\sigma)$ graphs, surface charge density representation and molecular model assigned. See text for details.

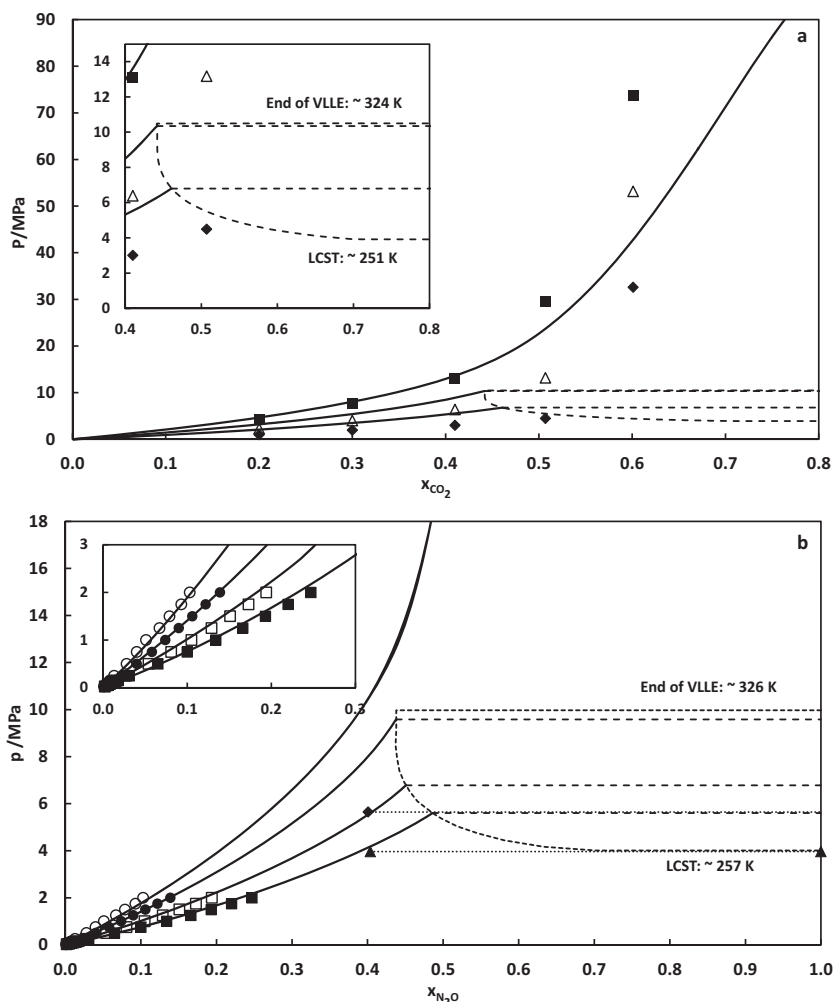


Fig. 3. Pressure-composition diagram of the binary systems. (a) $\text{CO}_2 + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (VLE: \blacklozenge , 293.42 K; \triangle , 323.09 K; \blacksquare , 369.13 K) and (b) $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ (VLE: \blacksquare , 283.13 K; \square , 298.11 K; \bullet , 323.15 K; \circ , 347.64 K, and VLLC: \blacktriangle , 283.2 K; \blacklozenge , 298.2 K). Symbols are experimental data [19,40] and the solid and the dashed lines represent the soft-SAFT EoS results for the VLE and the VLLC, respectively.

for the density description and for the binary systems phase equilibria prediction for the highest and lowest experimental temperatures available. For a fair comparison, no binary adjustable parameters were used. Set *A.XV* clearly provides the best $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ phase equilibria prediction and a similar satisfactory description of the $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ density and CO_2 solubility (excepting some deviations at very high pressures in the latter case), with deviations of 0.19% in density, of 39.2% in the CO_2 solubility and of 12.2% in the N_2O solubility. The values for the chain length, m_i , the segment diameter, σ_{ii} , and the dispersive energy between segments, ε_{ij}/k_B , from this set are in the same range than the values previously obtained for the $[\text{C}_4\text{mim}]^+$ ionic liquids with the $[\text{BF}_4]^-$ [21], the $[\text{NTf}_2]^-$ [22] and the $[\text{CH}_3\text{OHPO}_2]^-$ [28] anions.

Recently, Cláudio et al. [41] proposed an extended polarity scale of the ability of the ionic liquid anion to hydrogen-bond, through hydrogen-bonding interaction energies, occurring in equimolar cation–anion mixtures, calculated with COSMO-RS. The $[\text{N}(\text{CN})_2]^-$ anion presents higher hydrogen-bonding interaction energy than the $[\text{BF}_4]^-$ and the $[\text{NTf}_2]^-$ anions and lower hydrogen-bonding interaction energy than $[\text{CH}_3\text{OHPO}_2]^-$. Then, it is coherent that $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ association parameters values are higher than the ones previously reported for $[\text{BF}_4]^-$ [21] and $[\text{NTf}_2]^-$ [22,24] ionic liquids and lower than the ones of $[\text{C}_2\text{mim}][\text{CH}_3\text{OHPO}_2]^-$ [28].

Using this optimal set of parameters (reported in Table 1), it is possible to successfully extend the prediction results for mixtures for all the isotherms, between 283.13 K to 363.19 K of the

$\text{CO}_2/\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ systems (Fig. 3a and b). As can be seen, the model predicts again a liquid–liquid region for both systems with a LCST at a temperature of about 251 K for CO_2 and 257 K for N_2O . The existence of a LLE region at high concentrations in the N_2O system was also experimentally observed by Shiflett et al. [19]. In this IL, the end of the VLLC region, i.e. the temperature of the critical endpoint (CEP), is predicted around 324 K and 326 K for CO_2 and N_2O , respectively, having very similar areas.

2.3. $[\text{C}_4\text{mim}][\text{SCN}]$: molecular model and CO_2 and N_2O solubilities

The same procedure applied to determine the most appropriate molecular model and parameters of $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ was followed for $[\text{C}_4\text{mim}][\text{SCN}]$. As shown in Fig. 4, where COSMO-RS σ -profile $p(\sigma)$ graphs and surface charge density are depicted, the $[\text{SCN}]^-$ anion presents a peak around $1.5 \text{ e}/\text{\AA}^2$ and a smaller one around $0.75 \text{ e}/\text{\AA}^2$. These two near peaks can be related to the delocalization of the anion negative charge due to its resonance structure. Again, considering the cation and anion as a whole molecule, as in previous works, two association models were proposed to account for the $[\text{C}_4\text{mim}][\text{SCN}]$ interactions in the liquid, using only one or two associating sites, as represented in Fig. 4. Both hypotheses are reasonable: a priori, two association sites would represent the delocalized charge, but as the second peak is narrow and close to the main one, it can also be assumed that one

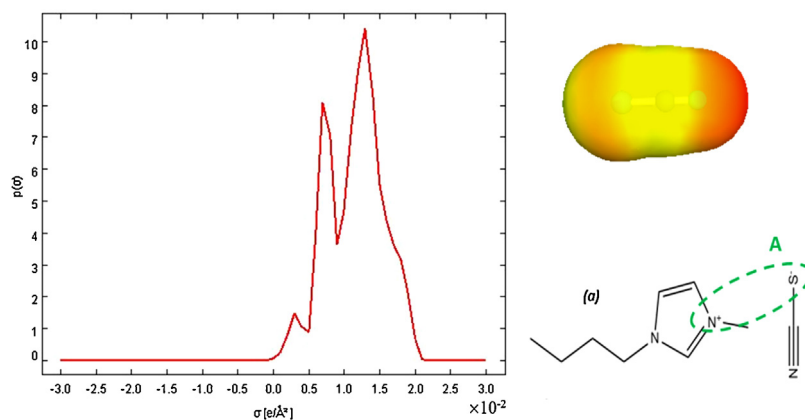


Fig. 4. [C₄mim][SCN] σ -profile $p(\sigma)$ graphs, surface charge density representation and molecular model assigned. See text for details.

associating site will be enough to consider the main hydrogen-bonding interactions. We would like to insist here on the idea of proposing approximate mesoscopic coarse-grained simple models for practical applications, relying on the fundamental physics behind soft-SAFT.

Chen et al. [30] also considered one association site in the [C₄mim][SCN] and, as for [C₄mim][N(CN)₂], no details were given about this choice.

Molecular parameters for both association schemes were regressed from liquid density data at atmospheric pressure [42,43] and the different sets obtained were evaluated on their ability to predict the solubility of CO₂/N₂O in [C₄mim][SCN] by comparing to the available data. Experimental CO₂ and N₂O solubilities in this ionic liquid were measured by Revelli et al. [20,44] in a wide range of temperature (293–383 K) and by Shiflett et al. [19] for a single temperature (298 K).

As expected, several sets allowed a good description of the density data points and the best one was chosen by checking their performance for high pressure binary data. When the different sets obtained were applied to predict the experimental data by Revelli et al. [20,44] for the CO₂ and the N₂O solubilities in [C₄mim][SCN], considerable deviations were obtained when modeling the N₂O + [C₄mim][SCN] phase behavior. A comparison of the experimental solubility measured by Revelli et al. [20,44] and Shiflett et al. [19] reveals that both measurements are in relative good agreement for CO₂ but not for N₂O. Consequently, the experimental points measured by Revelli et al. were dropped and the following calculations were focused only on the experimental data by Shiflett et al. [19].

Results considering only one association site on the IL are listed in Table S2, while the results when considering two association sites are listed in Table S3, both at the Supporting Info. The best sets of molecular parameters in terms of the density description and binary mixtures high pressure phase equilibria for each association scheme considered perform equally well. Consequently, although any of the two choices would be acceptable, we have prioritized the simpler scheme with only one association site, being proposed to represent the [C₄mim][SCN] ionic liquid with soft-SAFT. Set B.XIII can describe the IL density with deviations of 0.10% and successfully predict the N₂O solubility in [C₄mim][SCN] with deviations inferior to 8%. As some deviations were still found for the CO₂ solubility, a temperature independent binary interaction parameter ξ of 0.98 was used to improve the calculations and reach better agreement with the experimental data (Fig. 5a and b), with deviations of 5%. This final set of parameters has been included in Table 1.

Looking to the Cláudio et al. [41] extended polarity scale, the [SCN][−] and the [N(CN)₂][−] anions present close values of

their hydrogen-bonding interaction energies, somehow justifying the similar values obtained for their association parameters. m , σ and ε_{ii}/k_B values are also in agreement with the previous results obtained when applying soft-SAFT to [C₄mim]⁺ ionic liquids [20,21].

Finally, it is important to remark that once more the model predicts liquid–liquid immiscibility for both gases. The LCST is roughly at 233 K for CO₂ and 252 K for N₂O, whereas the end of the VLLE region is predicted at a CEP temperature of 327 K for both gases. No experimental data for the VLLE were available for these systems with [C₄mim][SCN].

2.4. [C₄mim][Ac]: molecular model and CO₂ and N₂O solubilities

[C₄mim][Ac] is the last ionic liquid belonging to a different anion family studied in this work with soft-SAFT. The [Ac][−] σ -profile ($p(\sigma)$) presents two major peaks, one around $2 e/\text{Å}^2$ and another close to $0.25 e/\text{Å}^2$ (Fig. 6), representing the anion O[−] atom and the delocalized charge due to the second O[−] atom present in the anion. Following the coarse grained scheme previously explained, and considering that the second peak is very broad, the [C₄mim][Ac] pair was modeled considering two associating sites, one A site which would mimic the O[−] atom interactions with the cation, and one B site representing the delocalized charge due to the second O[−] atom on the anion, as depicted in Fig. 6.

As previously, several molecular parameters sets regressed from atmospheric pressure liquid density data [45] were obtained, and the best set was evaluated through the ability to accurately predict the N₂O solubility in [C₄mim][Ac], measured by Shiflett et al. [18] at four different temperatures from 283.14 K to 347.71 K. The same authors also presented the CO₂ solubilities in this ionic liquid. This system is characterized by an unusual phase behavior, with very high solubilities of CO₂ in [C₄mim][Ac] being noticed at low pressures. This behavior is explained by the chemisorption taking place in [C₄mim][Ac] at low CO₂ pressures [46–48]. This chemical process can be taken into account within the soft-SAFT framework by considering cross-association between CO₂ and the IL, as will be further explained in detail. Nevertheless, since the [C₄mim][Ac] + CO₂ system requires a different modeling approach, and in order to follow an equal procedure for the parameters evaluation for all the considered ILs, it was decided not to use the CO₂ solubility data in [C₄mim][Ac] in the parameters values selection.

The best suitable sets of parameters are listed in Table S4, with set D.XXIII stepping out on the accurate description of the liquid density data and prediction of the high pressure phase behavior of the N₂O + [C₄mim][Ac] system at the lowest and at the highest available temperatures, with deviations of 0.04% and of 17.7% for pure liquid densities and N₂O solubilities, respectively.

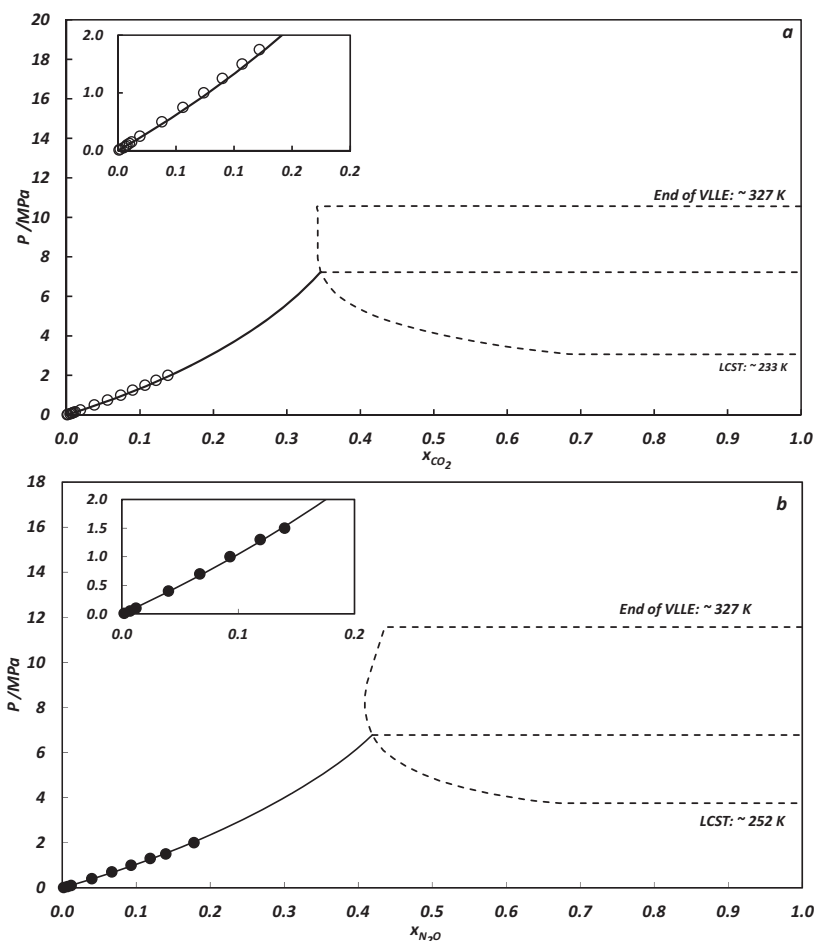


Fig. 5. Pressure-composition diagram at 298 K of the binary system. (a) $\text{CO}_2 + [\text{C}_4\text{mim}][\text{SCN}]$ and (b) $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{SCN}]$. Symbols are experimental data [19] and the solid and the dashed lines represent the soft-SAFT EoS results for the VLE and the VLLE, respectively.

The chain and reference term parameters values are again within the range of those obtained for the other $[\text{C}_4\text{mim}]^+$ ionic liquids. The association parameters values, $\varepsilon_{ii}^{\text{HB}}/k_B$ and K_{ii}^{HB} , are equal to the ones for the $[\text{C}_2\text{mim}][\text{CH}_3\text{OHPO}_2]$ ionic liquid. Acetate and phosphonate type anions lead the extended polarity scale [41], suggesting that these highly polar ionic liquids can be characterized by the same association parameters values, the highest used to model ILs in the soft-SAFT framework up to now. The optimal set of values is included in Table 1.

The predictive ability of set *D.XXIII* of molecular parameters for $[\text{C}_4\text{mim}][\text{Ac}]$ can be successfully extended for the

intermediate temperatures for which the N_2O solubility data were reported by Shiflett et al. [18], as depicted in Fig. 7a. Liquid–liquid immiscibility also appears, even at lower N_2O compositions than for the other ILs, in accordance with the experimental data points available at 282.65 K and 292.95 K. A LCST and end of the VLLE region at about 252 K and 325 K, respectively, is also anticipated by the model.

Having selected the association scheme and the molecular parameters values, the next step is to describe the phase equilibria of the $\text{CO}_2 + [\text{C}_4\text{mim}][\text{Ac}]$ system reported by Shiflett et al. [18] at four different temperatures from 283.10 to 343.10 K.

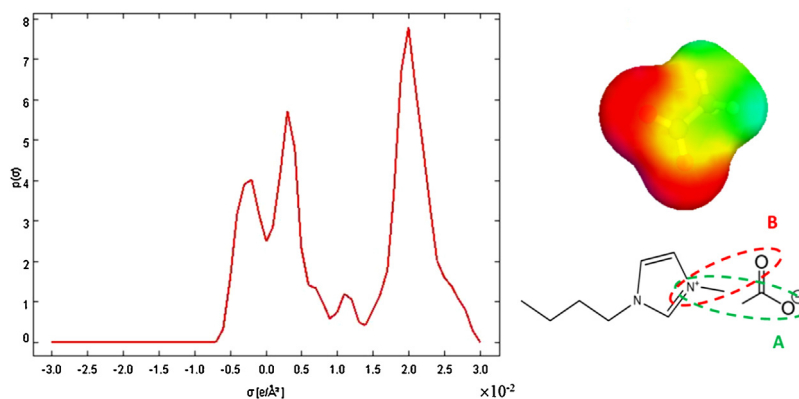


Fig. 6. $[\text{C}_4\text{mim}][\text{Ac}]$ σ -profile $p(\sigma)$ graphs, surface charge density representation and molecular model assigned. See text for details.

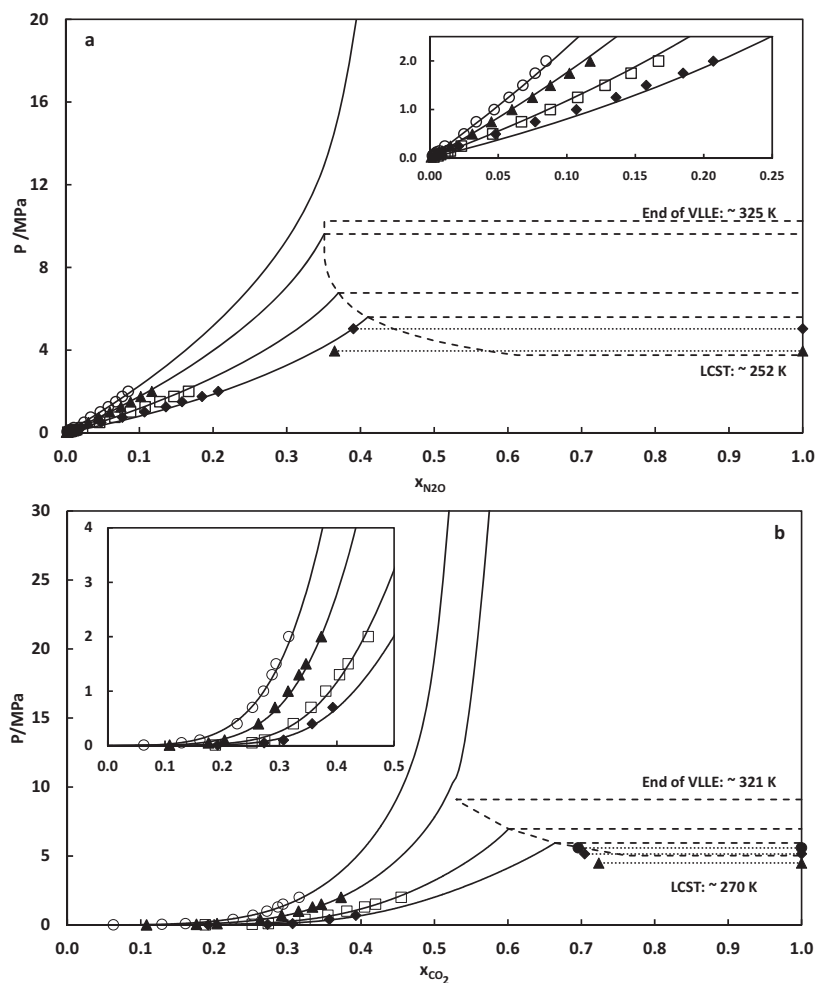


Fig. 7. Pressure-composition diagram of the binary system. (a) $\text{CO}_2 + [\text{C}_4\text{mim}][\text{Ac}]$ (VLE: \blacklozenge , 283.10 K; \square , 298.10 K; \blacktriangle , 323.10 K; \circ , 343.10 K; and VLLE: \blacktriangle , 281.1 K; \blacklozenge , 288.7 K; \bullet , 292.2 K) and (b) $\text{N}_2\text{O} + [\text{C}_4\text{mim}][\text{Ac}]$ (VLE: \blacklozenge , 283.14 K; \square , 298.11 K; \blacktriangle , 323.14 K; \circ , 347.71 K; and VLLE: \blacktriangle , 282.65 K; \blacklozenge , 292.95 K). Symbols are experimental data [18] and the solid and the dashed lines represent the soft-SAFT EoS results for the VLE and the VLLE, respectively.

Association equations of state, like soft-SAFT, are able to deal with some particular reacting systems through the association theory of Wertheim. This is done by incorporating associating sites, or in this specific case reacting sites, in the molecules involved, as done by some authors. In 2008, Belkadi et al. [49] used the soft-SAFT EoS to successfully describe the NO_2 dimerization reaction by including one associating site in the molecule. The nature of the dimerization reaction was further correctly taken into consideration with soft-SAFT through the use of a large cross-association energy and a small cross-associating volume values, while the amount of N_2O_4 could be calculated through the fraction of aggregates, which can be directly obtained from any SAFT equation. Mac Dowell et al. [50] described the CO_2 solubility in monoethanolamine with the SAFT-VR EoS considering CO_2 as a non-self-associating molecule, but able to associate with the alkanolamine. Two associating sites were considered in the CO_2 to represent the interaction of the amine electron lone-pair with the electron-depleted carbon in the CO_2 . In later works, the same approach was successfully used for other multifunctional alkanolamines [51,52]. A similar approach is here applied with soft-SAFT for the description of the high pressure phase equilibria of the $\text{CO}_2 + [\text{C}_4\text{mim}][\text{Ac}]$ system.

Taking into account the chemical reaction scheme first proposed by Maggin et al. [53] and further detailed by Cabaço, Besnard and co-workers [46–48], the reversible CO_2 reaction with $[\text{C}_4\text{mim}][\text{Ac}]$ takes place between the carbon electron lone-pair and one of the double bounds of the CO_2 molecule. This suggests that the adequate

approach would be to adopt two possible associating sites in the CO_2 molecule that interact with one site of the IL cation. Preliminary results considering one associating site in the CO_2 (not shown here) were not able to accurately reproduce the unusual curve of the CO_2 solubility in $[\text{C}_4\text{mim}][\text{Ac}]$. A very good description of the experimental data was achieved when assuming two associating sites in the CO_2 , representing the two double bounds were the reaction can take place. The assumption of two associating sites in the CO_2 was also adopted by Mac Dowell et al. with the SAFT-VR to describe the chemical reaction between CO_2 and monoethanolamine [50].

An optimization of the best values for the cross-association parameters was done, always in a logical range according to the physical interpretation of the chemical reaction. A very high cross-association energy value is expected, simulating the very strong interaction of a covalent bond, while the volume of association is expected to be small, as the reaction will be localized in a specific place of the molecule. Having this in mind, final values of 950 \AA^3 for the bonding volume and of 5500 K for the cross-associating energy were chosen. Finally, the energy binary interaction parameter, ξ_{ij} , was fitted to each isotherm, and found to follow a linear dependency with the temperature represented by Eq. (1).

$$\xi = -0.0017M_w + 1.463 \quad (1)$$

As depicted in Fig. 7b, the unusual phase equilibria of the $\text{CO}_2 + [\text{C}_4\text{mim}][\text{Ac}]$ system, including the very large CO_2 solubility at small concentrations, is quantitatively described with soft-SAFT for

Table 2
Henry's law constants (MPa) and selectivities for CO₂ and N₂O in the selected ionic liquids.

	H _{CO₂} [19]	H _{N₂O} [19]	H _{CO₂} ^a	H _{N₂O} ^a	S _{CO₂/N₂O} ^a
298 K					
[C ₄ mim][BF ₄]	5.38	7.86	7.60	8.60	1.13
[C ₄ mim][NTf ₂]	1.62	3.21	3.05	3.24	1.06
[C ₄ mim][N(CN) ₂]	4.06	8.69	8.86	9.11	1.03
[C ₄ mim][SCN]	10.28	12.78	12.02	9.66	0.80
[C ₄ mim][Ac]	0.053	10.92	0.027	10.94	400.71
303 K					
[C ₄ mim][BF ₄]	6.32	7.79	8.49	9.35	1.10

^a This work.

the four temperatures for which experimental data are available. Also, in agreement with the experimental VLE points available at 281.1 K, 288.7 K and 292.2 K [18], liquid–liquid immiscibility at high CO₂ concentrations is predicted. A LCST and a CEP at about 270 K and 321 K, respectively, are estimated with the soft-SAFT EoS.

As mentioned previously, Table 1 summarizes the best molecular parameters sets assigned for each [C₄mim]⁺ ionic liquid studied in this work. As additional information, Fig. 8 depicts the correspondent liquid density modeling results for the three new studied ILs.

2.5. Henry's law constants and selectivities

Using the parameterization discussed above, the soft-SAFT was further applied to estimate the Henry's law constants for the two gases in each ionic liquid here investigated. The Henry's law relates the amount of a given gas dissolved in a liquid at a constant temperature to the fugacity of that gas in equilibrium with that liquid:

$$H_{i,L}(T, p) = \lim_{x_i \rightarrow 0} \frac{f_i^L}{x_i} \quad (2)$$

The limiting slope as the solubility approaches zero is calculated through the equation of state phase equilibria results. Henry's law constants for the studied gases in the selected ionic liquids, at 298 K and 303 K, are reported in Table 2. The values are in agreement with those reported in the literature [19,54] and also presented for comparison in Table 2. Henry's law constants for CO₂ in the same ionic liquids were slightly lower than for N₂O (except for [C₄mim][SCN]) suggesting that it is the more soluble gas. This

difference is quite significant for [C₄mim][Ac], in agreement with the higher solubility of CO₂ in this IL due to the chemical absorption observed in this system.

Once all gases Henry's law constants in the different solvents are estimated, gas selectivity can be easily calculated for all the ionic liquids as the ratio between the Henry's law constants for each gas:

$$S_{\text{CO}_2/\text{N}_2\text{O}} = \frac{H_{\text{N}_2\text{O}}}{H_{\text{CO}_2}} \quad (3)$$

Results for all the ionic liquids are also displayed in Table 2. Except for [C₄mim][Ac], low CO₂/N₂O selectivities are obtained in the rest of the cases. These low selectivities are expected considering the CO₂ and N₂O similar solubilities in these ILs, and confirmed by the similar Henry's law constants values found. From these results, it is concluded that the anions [N(CN)₂]⁻, [SCN]⁻, [BF₄]⁻ and [NTf₂]⁻ have similar affinities with CO₂ and N₂O and are not recommended for CO₂/N₂O separation. Conversely, [C₄mim][Ac] presents a much higher selectivity toward CO₂, related to the chemical absorption of CO₂ versus the physical absorption of N₂O, indicating that this ionic liquid is a potential candidate to separate CO₂/N₂O mixtures.

3. Conclusions

The development of thermodynamic models able to describe the high pressure vapor–liquid equilibrium of different ILs + gas systems is a mandatory requirement for the development and implementation of separation and capture processes using ILs. In this work, the soft-SAFT equation has been used to predict the carbon dioxide and the much less studied nitrous oxide solubilities in [C₄mim]⁺ ionic liquids with different anions. Besides the well-studied [BF₄]⁻ and [NTf₂]⁻, other anions addressed have included [N(CN)₂]⁻, [SCN]⁻ and [Ac]⁻.

Following our previous approach, the ionic liquids were modeled as an ion pair. The molecular models and association schemes for the different ionic liquids were proposed based on the guidance of COSMO-RS quantum calculations and previous experience; specific molecular models were assigned for each ionic liquid belonging to a different anion family: [C₄mim][N(CN)₂] and [C₄mim][Ac] were described with two association sites and [C₄mim][SCN] with one, while the literature models were used in a transferable manner for the previously studied ILs with [BF₄]⁻ and [NTf₂]⁻ anions, with one and three association sites, respectively.

In a first stage, the N₂O solubilities on [C₄mim][BF₄] and [C₄mim][NTf₂] anions were modeled using a single temperature independent binary interaction parameter, having the same value for both ILs and very close to that used for CO₂ in previous contributions [22,24]. Very good agreement with the experimental data was achieved at all temperatures, allowing predictions at higher concentrations. Liquid–liquid immiscibility was reported for both

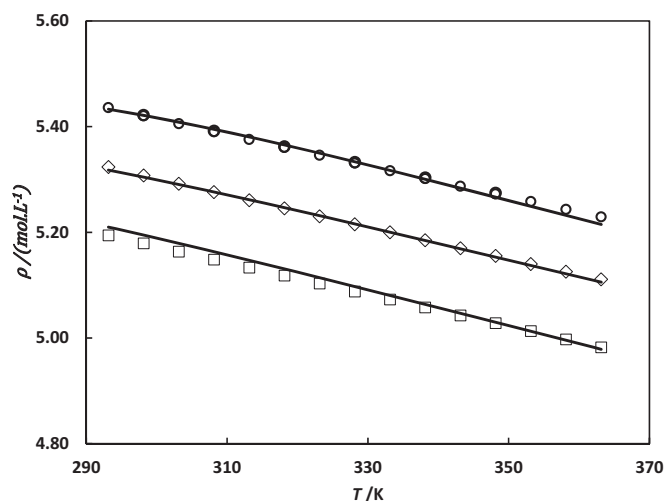


Fig. 8. Temperature–density diagrams for [C₄mim][N(CN)₂] [39] (□), [C₄mim][SCN] [42,43] (○) and [C₄mim][Ac] [45] (◇). The solid lines represent the soft-SAFT EoS fit.

ionic liquids at high N₂O concentrations, in agreement with the suggestions of Shiflett et al. [19,37].

In a second stage, the new [C₄mim][N(CN)₂], [C₄mim][SCN] and [C₄mim][Ac] ILs were addressed. Once the molecular models were established, different sets of ionic liquids molecular parameters were determined and the best for each compound was identified from considering ILs pure liquid densities and the ability to describe CO₂ and N₂O solubilities at high pressures. The correspondent association molecular parameters values were also evaluated and found to be in agreement with the anion polarity. The adequacy of the proposed molecular models and parameters values was further confirmed by the description of the phase equilibria using a predictive approach (no binary interaction parameters used) of all the N₂O systems, at several temperatures. CO₂ solubility was predicted for [C₄mim][N(CN)₂], while a temperature independent binary interaction parameter close to unity was used for [C₄mim][SCN]. For [C₄mim][Ac], the particular phase equilibrium of its mixture with CO₂ due to a chemisorption process, was addressed through the representation of this chemical reaction by a cross-associating scheme involving the addition of two association sites in the CO₂ only able to cross-associate with the IL.

In all cases, liquid–liquid immiscibility was found at high gas concentrations, being possible to determine the whole VLE region for each system, and giving insight in a region where less experimental data are available.

Finally, the CO₂ and N₂O Henry's law constants in the [C₄mim] ionic liquids were predicted with soft-SAFT. With the exception of [C₄mim][Ac], very low CO₂/N₂O selectivities were reported for the ILs, not being recommended for this gas separation. On the contrary, [C₄mim][Ac] selectivity toward CO₂ is several orders of magnitude higher than for N₂O, showing that this IL can be used for a practical separation of CO₂/N₂O mixtures.

This work is an example of the use of soft-SAFT as a modeling tool to provide quick answers about the thermodynamic feasibility of a specific solvent for a particular application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.supflu.2014.06.005>.

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