

# Application of a group contribution equation of state for the thermodynamic modeling of the binary systems CO<sub>2</sub>–1-butyl-3-methyl imidazolium nitrate and CO<sub>2</sub>–1-hydroxy-1-propyl-3-methyl imidazolium nitrate

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## ARTICLE INFO

### Article history:

Received 30 March 2008

Received in revised form 2 May 2009

Accepted 3 May 2009

### Keywords:

Ionic liquids

Carbon dioxide

Phase behavior

Group contribution equation of state

## ABSTRACT

It is known that the properties of ionic liquids (ILs) can be tuned by appropriate selection of cations and anions. Even when an infinite number of ionic liquids can be generated, only a limited number of families of anions and cations are used. The group contribution equation of state (GC-EoS) is a promising method for calculating the phase behavior of the ILs. If the parameters of the characteristic functional group of a family are fitted by using data of a reduced number of ILs of the family, the phase behavior of all the ILs of the same family can be predicted using exclusively the data of the pure component. Previously, the parameters of the IL families with an imidazolium-based cation and the anions PF<sub>6</sub>, BF<sub>4</sub> and Tf<sub>2</sub>N have been fitted to experimental data. In this work, the GC-EoS has been used to calculate the CO<sub>2</sub>–IL phase behavior of two ionic liquids with an imidazolium-based cation and a nitrate anion: 1-butyl-3-methyl imidazolium nitrate (BMImNO<sub>3</sub>) and 1-hydroxy-1-propyl-3-methyl imidazolium nitrate (HOPMImNO<sub>3</sub>). To fit the parameters of the functional group 3-methyl imidazolium nitrate (MImNO<sub>3</sub>), experimental activity coefficients at infinite dilution ( $\gamma^\infty$ ) of the BMImNO<sub>3</sub> with alkanes and alcohols are used together with the experimental data. The average error of the calculated bubble points is 2.6% in pressure for the system CO<sub>2</sub>–BMImNO<sub>3</sub> and 6.7% for the system CO<sub>2</sub>–HOPMImNO<sub>3</sub>. The activity coefficients at infinite dilution ( $\gamma^\infty$ ) are predicted with an average deviation of 6.9%.

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## 1. Introduction

Ionic liquids (ILs) are liquids that are composed entirely of ions. They are liquid at ambient or close-to-ambient temperature. They are receiving increasing attention as solvents for reaction processes [1]. This interest stems from their potential as “green” solvents. Their non-volatile character, high thermal and chemical stability and recoverability make them potentially attractive alternatives over environmentally unattractive organic solvents, in particular in comparison with chlorinated hydrocarbons [2]. They are good solvents for a wide range of both inorganic and organic materials. Moreover, all their properties can be tuned by appropriate modifications of the cation, anion or both.

Supercritical carbon dioxide (scCO<sub>2</sub>) has been found to be able to extract or precipitate substances from an ionic liquid without any cross-contamination [3–6]. As an additional feature, CO<sub>2</sub> is able to force two or more immiscible phases to form one homogeneous phase upon pressure increase [7–9] and, in reverse, to split a homogeneous fluid phase into two or three phases upon pressure decrease. This phenomenon is called miscibility switch [10,11], and can be applied in combined reaction and separation systems for performing monophasic or biphasic reactions.

Due to the advantages of using CO<sub>2</sub> in reactions and phase separations, an increasing interest in the knowledge of the phase behavior of CO<sub>2</sub>–IL systems has developed. The phase behavior of different IL–CO<sub>2</sub> systems shows some common features, i.e. large quantities of CO<sub>2</sub> dissolve in the ILs but no measurable amounts of the ILs dissolve in the CO<sub>2</sub> [6]. Experiments performed at very high pressures proved that, instead of reaching a critical point in an isothermal pressure–composition diagram, the phase envelope does not close, even at pressures as high as 100 MPa and CO<sub>2</sub> concentrations up to 70 mol% for various imidazolium-based ILs with PF<sub>6</sub> and BF<sub>4</sub> anions [12–17]. Considering the large variety of ionic

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liquids that may be formed, methods to predict their phase behavior are needed. A lot of work in this field was developed over the last years, and here only a few of them are mentioned. A number of methods using molecular simulation [18–27] were developed in order to explain and predict phase equilibrium and properties of ILs. Excess Gibbs models such as NRTL [28–32] and UNIQUAC [28] were developed for describing both LL and LV equilibrium. Nevertheless, the calculation of phase behavior using an equation of state (EoS) has been less explored. Shariati and Peters [33] used a Peng–Robinson equation of state to model the high-pressure phase behavior of the system fluorofrom + 1-ethyl-3-methyl imidazolium hexafluorophosphate. Although the PR EoS is certainly not a suitable way to describe this system, it is able to satisfactorily model the solubility of the supercritical fluid in the IL and describe and predict qualitatively the solubility of the ionic liquid in supercritical  $\text{CHF}_3$ . Shiflett and Yokozeki [34–37] modeled the phase behavior of systems IL– $\text{CO}_2$  up to 2 MPa using a generic Redlich–Kwong type of cubic equation of state. Other authors used different EoS incorporating the “group contribution concept”, that is, if the parameters of the characteristic functional group of a family of ILs are fitted by using data of a reduced number of ILs of the family, the phase behavior of all the ILs of the same family can be predicted using exclusively the data of the pure components. Kim et al. [38,39] used a group contribution non-random lattice–fluid EoS to predict the solubilities of gases in several ionic liquids at pressures up to 1 MPa obtaining, in general, good agreement with experimental data. The vapor–liquid equilibria of binary systems containing imidazolium-based ionic liquids (ILs) were also modeled using a square-well chain fluids model (SWCFs). The homonuclear model [40] was improved by a heteronuclear model [41] where the ILs are represented by “diblock compounds”, with the alkyl group as one block and the imidazolium ring–anion pair as the other block. Model parameters of the imidazolium ring–anion block were obtained by fitting the experimental pressure–volume–temperature (PVT) data of the ILs, and they were combined with those of the alkyl block to correlate and predict the molar volumes of homologous imidazolium ILs. All of these EoS focus on describing the phase behavior of the IL at relatively low pressures. Other EoS were able to describe the anomalous behavior of the system  $\text{CO}_2$  + IL at very high pressure: the tPC SAFT was used for predicting the phase behavior of binary and multicomponent systems involving ILs [42–44] and binary systems  $\text{CO}_2$ –IL using soft-SAFT [45]. The SAFT models were able to capture the sharp increase of pressure as the solubility of  $\text{CO}_2$  increased, being the last model able to do so without assuming specific interactions between the  $\text{CO}_2$  and the IL.

In the present study a group contribution equation of state, the group contribution equation of state (GC-EoS) developed in the 1980s by Skjold–Jørgensen [46,47], was used to represent the phase behavior of the binary systems of the 1-alkyl-3-methyl imidazolium nitrate ionic liquid family and  $\text{CO}_2$ , following the methodology developed by Breure et al. [48] for the alkyl-3-methyl imidazolium hexafluorophosphate and alkyl-3-methyl imidazolium tetrafluoroborate IL families and  $\text{CO}_2$ . This EoS was also used to describe the phase behavior of ILs of the 1-alkyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide family in combination with several gases [49]. Besides the group contribution model being able to calculate the data of a complete family of ILs by fitting a reduced number of parameters to a few members of the family, Breure et al. [48] showed that a relatively simple model could describe the anomalous high-pressure behavior  $\text{CO}_2$  + IL system.

The objective of this work is to extend the GC-EoS to systems containing ionic liquids of the 1-alkyl-3-methyl imidazolium nitrate family and  $\text{CO}_2$ . To do so, new pure group parameters and binary interaction parameters for the new functional group 3-methyl imidazolium nitrate (MImNO<sub>3</sub>) were estimated on the basis of experimental information about the ILs of this family found in

literature and experimental values of infinite dilution activity coefficients of the BMImNO<sub>3</sub> in several alkanes and alcohols.

## 2. GC-EoS model

The GC-EoS was proposed by Skjold–Jørgensen [46,47] to calculate vapor–liquid equilibria of non-ideal mixtures at pressures up to 30 MPa. It is based on the generalized van der Waals function combined with the local composition principle. It is expressed in terms of the residual Helmholtz energy ( $A^R$ ) as the addition of an attractive term and a free volume contribution:

$$\left(\frac{A^R}{RT}\right)_{T,V,n} = \left(\frac{A^R}{RT}\right)_{\text{att}} + \left(\frac{A^R}{RT}\right)_{\text{fv}} \quad (1)$$

where  $V$  is the total volume,  $n$  is the total number of mol,  $R$  is the gas constant and  $T$  is the temperature.

The free volume (fv) term is described by the Mansoori and Leland expression for hard spheres:

$$\left(\frac{A^R}{RT}\right)_{T,V,n} = 3 \left(\frac{\lambda_1 \lambda_2}{\lambda_3}\right) (Y - 1) + \left(\frac{\lambda_2^3}{\lambda_3^2}\right) (Y^2 - Y - \ln Y) + n \ln Y \quad (2)$$

where

$$\lambda_k = \sum_j^{NC} n_j d_j^k$$

$$Y = \left(\frac{1 - \pi \lambda_3}{6V}\right)^{-1}$$

with  $n$  being the total number of moles,  $NC$  being the number of components,  $V$  being the total volume, and  $d$  being the hard-sphere diameter per mole.

The hard-sphere diameter  $d$  is assumed to be a function of the temperature:

$$d = 1.065655d_c \left(1 - 0.12 \exp\left(\frac{-2T_c}{3T}\right)\right) \quad (3)$$

where  $d_c$  is the value of the hard-sphere diameter at the critical temperature  $T_c$  for the pure component.

The attractive part of  $A^R$  is a group contribution version of a density dependent NRTL type expression:

$$\left(\frac{A^R}{RT}\right)_{\text{att}} = -\frac{z}{2} \frac{\sum_{i=1}^{NC} n_i \sum_{j=1}^{NG} v_j^i q_j \sum_{k=1}^{NG} \theta_k (g_{kj} q \tau_{kj} / RTV)}{\sum_{l=1}^{NG} \theta_l \tau_{lj}} \quad (4)$$

where

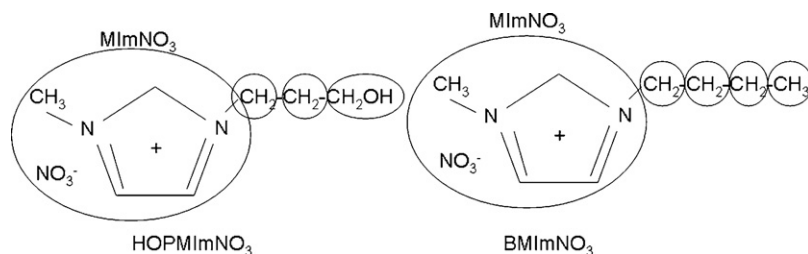
$$\theta_k = \frac{q_k}{q} \sum_{i=1}^{NC} n_i v_k^i q = \sum_{i=1}^{NC} n_i \sum_{j=1}^{NG} v_j^i q_j \quad (5)$$

$$\tau_{kj} = \exp\left(\frac{\alpha_{kj} \Delta g_{kj} q}{RTV}\right) \quad (6)$$

$$\Delta g_{kj} = g_{kj} - g_{jj} \quad (7)$$

In Eq. (4),  $z$  is the number of nearest neighbors to any segment (set equal to 10);  $v_j^i$  is the number of groups  $j$  in component  $i$ ;  $q_j$  is the number of surface segments assigned to group  $j$ ;  $\theta_k$  is the surface fraction of group  $k$ ;  $q$  is the total number of surface segments;  $g_{ij}$  is the attractive energy parameter for interactions between segments  $j$  and  $i$ ; and  $\alpha_{ij}$  is the corresponding non-randomness parameter. The interactions between unlike segments are defined by:

$$g_{ji} = k_{ji} \sqrt{g_{ii} g_{jj}} \quad (8)$$



**Fig. 1.** Decomposition of the ionic liquids 1-hydroxy-propyl-3-methyl imidazolium nitrate (HOPMImNO<sub>3</sub>) and 1-butyl-3-methyl imidazolium nitrate (BMImNO<sub>3</sub>) into separate functional groups.

where  $k_{ji}$  is a binary interaction parameter. In Eqs. (9) and (10) the temperature dependence assumed for the attractive energy parameter and the binary interaction parameter are:

$$g_{ii} = g_{ii}^* \left[ 1 + g'_{ii} \left( \frac{T}{T_i^* - 1} \right) + g''_{ii} \ln \left( \frac{T}{T_i^*} \right) \right] \quad (9)$$

$$k_{ij} = k_{ij}^* \left[ 1 + k'_{ij} \ln \frac{T}{T_{ij}^*} \right] \quad (10)$$

where  $T_{ii}^* = 0.5(T_i^* + T_j^*)$  and  $T_{ii}^*$  is an arbitrary but fixed reference temperature for the group  $i$ .

### 3. Thermodynamic modeling

In this work, pure group and binary interaction parameters for the new functional group 3-methyl imidazolium nitrate (MImNO<sub>3</sub>) were estimated on the basis of experimental information for the ionic liquids 1-butyl-3-methyl imidazolium nitrate (BMImNO<sub>3</sub>) and 1-hydroxy-1-propyl-3-methyl imidazolium nitrate (HOPMImNO<sub>3</sub>), experimental bubble points of the systems CO<sub>2</sub> + HOPMImNO<sub>3</sub> and CO<sub>2</sub> + BMImNO<sub>3</sub> [50] and experimental values of infinite dilution activity coefficients using the BMImNO<sub>3</sub> as solvent and several alkanes and alcohols as solutes. These coefficients were experimentally determined by Gloria Foco according to the method described in literature [51,52] and are presented for the first time in this work.

#### 3.1. Ionic liquid functional groups

In order to apply the GC-EoS, the pure components must be decomposed into separate functional groups. The CO<sub>2</sub> is a functional group itself. The ionic liquids of the 1-alkyl-3-methyl imidazolium nitrate family were decomposed into separate functional groups according to the methodology of Breure et al. [48] as shown in Fig. 1.

#### 3.2. Parameterization of the free volume term

The free volume term of the residual Helmholtz energy contains only one characteristic parameter, that is, the critical hard-sphere diameter ( $d_c$ ). Values for  $d_c$  are usually calculated from critical properties, or by fitting the equation to vapor pressure data. One of the main characteristics of ionic liquids is their negligible vapor pressure, thus this information is not available for most ionic liquids. In this work, the  $d_c$  was calculated by two methods: firstly from the critical properties estimated using the method developed by Valderrama and Robles [53] who obtained a value of  $d_c = 6.3636$  cm/mol for the BMImNO<sub>3</sub> and  $d_c = 6.2002$  cm/mol for the HOPMImNO<sub>3</sub>. Secondly, the  $d_c$  values were calculated in the same way as Breure et al. [48] using the correlation developed by Espinosa et al. [54,55] between the critical diameter  $d_c$  and the normalized van der Waals molecular volume ( $r$ ) of high molecular weight compounds, obtaining values of  $d_c = 6.009$  cm/mol for

the BMImNO<sub>3</sub> and  $d_c = 5.886$  cm/mol for the HOPMImNO<sub>3</sub>. Predictions of the LV data were not satisfactory using either of these estimated critical diameters, because it was not possible to find parameters that represented both systems with the same accuracy. Good predictions of the LV data of both ILs were obtained by adjusting the values of  $d_c = 6.0698$  cm/mol for the BMImNO<sub>3</sub> and  $d_c = 6.424$  cm/mol for the HOPMImNO<sub>3</sub>. These values of  $d_c$  were within the range of uncertainty of those estimated by the methods above described.

#### 3.3. Parameterization of the attractive term

The following parameters are required in order to calculate the attractive term of the GC-EoS:

- (i) Pure group constants:  $T_{ii}^*$ ,  $q_i$
- (ii) Pure group energy parameters:  $g_{ii}^*$ ,  $g'_{ii}$ ,  $g''_{ii}$
- (iii) Group–group interaction parameters:  $k^*$ ,  $k'_{ij}$ ,  $\alpha_{ij}$ ,  $\alpha_{ji}$

Pure group parameters for the small functional groups were taken from Skjold-Jørgensen, those for CH<sub>3</sub>, CH<sub>2</sub> from [47] and CH<sub>2</sub>OH and CO<sub>2</sub> from [46]. Binary parameters for interactions between CO<sub>2</sub> and the paraffin groups were taken from Espinosa et al. [56] and those for the CH<sub>2</sub>OH group from Skjold-Jørgensen [46].

Pure group  $q_i$  constant for the group MImNO<sub>3</sub> was calculated using a group contribution approach as follows:

$$q_i = \sum_{k=1} v_k^{(i)} Q_k \quad (11)$$

where  $v_k^{(i)}$  is the number of groups  $k$  in the molecule when it is divided as shown in Fig. 2.

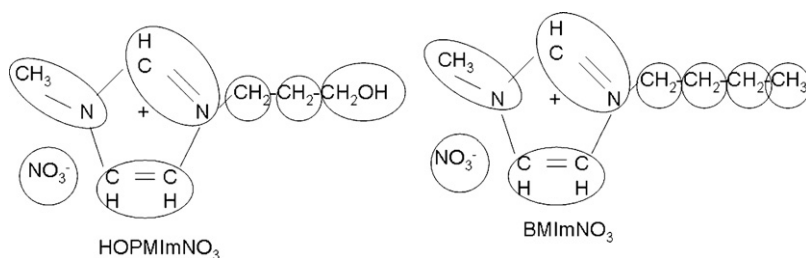
The group parameters  $Q_k$  represent the van der Waals surface area, normalized by a standard segment area of  $2.5 \times 10^5$  m<sup>2</sup>/mol, as in the UNIFAC model [57]. The area  $Q_k$  parameters of MImNO<sub>3</sub> functional group were calculated from the constituent units shown in Fig. 1. Table 1 contains  $Q_k$  of units and functional groups taken from literature [57–59].

$T_{ii}^*$  for the group MImNO<sub>3</sub> was fixed at 600 K. Pure group energy parameters and binary interaction parameters of this group

**Table 1**

Group contribution equation of state (GC-EoS) group surface area ( $Q_k$ ) parameters, where ImNO<sub>3</sub> is imidazolium nitrate.

Group or unit	$Q_k$	Source
CH <sub>3</sub>	0.848	[58]
CH <sub>2</sub>	0.540	[58]
CH=CH	0.867	[58]
CH <sub>3</sub> –N	0.940	[58]
CH=N	0.324	[58]
NO <sub>3</sub>	1.600	[59]
CH <sub>2</sub> OH	1.124	[57]
ImNO <sub>3</sub>	3.731	Calculated



**Fig. 2.** Functional groups used for decomposing the ionic liquids 1-hydroxy-propyl-3-methyl imidazolium nitrate (HOPMImNO<sub>3</sub>) and 1-butyl-3-methyl imidazolium nitrate (BMImNO<sub>3</sub>) in order to calculate the group surface area parameters ( $Q_k$ ).

and the functional groups CH<sub>3</sub>, CH<sub>2</sub>, and CH<sub>2</sub>OH were initially estimated by adjusting infinite dilution activity coefficients of alkanes and alcohols in the ionic liquid BMImNO<sub>3</sub> by minimizing Eq. (12).

$$F = \sum_{i=1}^{N\text{-data}} \left( \frac{\gamma_{i,al,calc}^{\infty}}{\gamma_{i,al,exp}^{\infty}} - 1 \right)^2 \quad (12)$$

The binary interaction parameters ( $k_{ij}$  and  $\alpha_{ij}$ ) between CO<sub>2</sub> and the MImNO<sub>3</sub> group were obtained by adjusting bubble point data of CO<sub>2</sub> in the ionic liquids HOPMImNO<sub>3</sub> and BMImNO<sub>3</sub>. The most suitable set of parameters for a given set of input data were those that minimized the average absolute pressure deviation (AAPD):

$$AAPD(\%) = 100 \sum_{i=1}^{N\text{-data}} \frac{|P_{exp} - P_{calc}|}{P_{exp}} \quad (13)$$

The obtained values were refined in order to improve the predictions of the EoS.

To keep the number of parameters as low as possible, the following fitting strategy was adopted:

- A linear temperature dependence was assumed for the attractive energy parameter  $g_{ii}$  (i.e.,  $g_{ii}'' = 0$ ).
- The same values were given to the binary interaction parameters of both paraffin groups CH<sub>3</sub> and CH<sub>2</sub>, since they are members of the same functional group family.
- The  $k_{ij}$  binary interaction parameter was considered to be temperature independent (i.e.  $k_{ij}' = 0$ ).

#### 4. Results

The GC-EoS new parameters determined by adjusting experimental data are reported in Tables 2–4. Table 2 shows the pure component parameters used. In Table 3, the parameters

**Table 2**

Group contribution equation of pure component parameter for the ionic liquids 1-hydroxy-propyl-3-methyl imidazolium nitrate (HOPMImNO<sub>3</sub>) and 1-butyl-3-methyl imidazolium nitrate BMImNO<sub>3</sub>.

	Pure component parameters		
	$T_c$ (K)	$d_c$ (cm/mol)	MW (g/mol)
BMImNO <sub>3</sub>	946.33	6.0698	201
HOPMImNO <sub>3</sub>	1004.932	6.424	204

**Table 3**

Adjusted group contribution equation of pure group parameter for the new functional group 3-methylimidazolium nitrate (MImNO<sub>3</sub>).

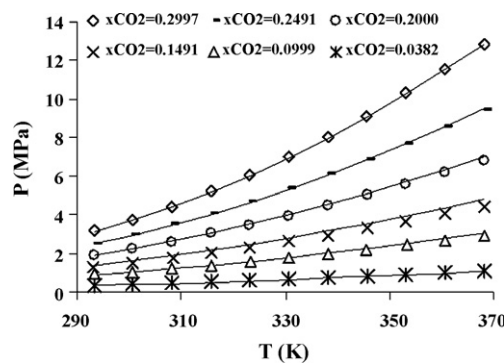
Group	Pure group parameters				
	$T^*$ (K)	$q$	$g^*$	$g'$	$g''$
MImNO <sub>3</sub>	600	3.731	1332740	-0.1775	0

**Table 4**

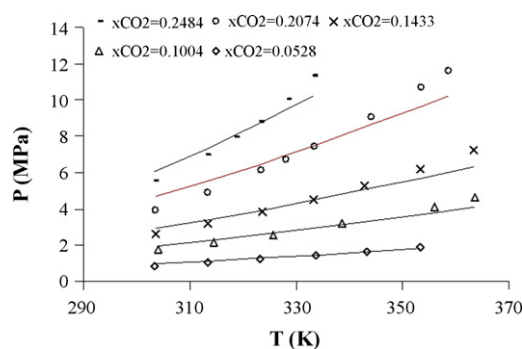
Adjusted group contribution equation of state binary interaction parameter for CO<sub>2</sub> + methyl imidazolium nitrate ionic liquid systems.

Binary interaction parameters					
$i$	$j$	$k_{ij}^*$	$k_{ij}'$	$\alpha_{ij}$	$\alpha_{ji}$
MImNO <sub>3</sub>	CH <sub>2</sub>	0.6500	0	0	0
MImNO <sub>3</sub>	CH <sub>3</sub>	0.6500	0	0	0
MImNO <sub>3</sub>	CO <sub>2</sub>	0.8235	0	-0.0033	-0.0033
MImNO <sub>3</sub>	CH <sub>2</sub> OH	1.1093	0	0	0

adjusted and calculated for the new functional group 3-methyl imidazolium nitrate (MImNO<sub>3</sub>) are listed. In Table 4, the fitted binary interaction parameters between the new functional group MImNO<sub>3</sub> and the other functional groups present in the system are shown. In Figs. 3 and 4, the calculated bubble points of the systems CO<sub>2</sub> + BMImNO<sub>3</sub> and CO<sub>2</sub> + HOPMImNO<sub>3</sub>, respectively, are compared with the experimental values. The average deviation of the calculated bubble points was 2.6% in pressure for the system



**Fig. 3.** Comparison of the experimental [50] bubble points of the system CO<sub>2</sub> + BMImNO<sub>3</sub> and the isopleths calculated by the GC-EoS. The symbols represent the experimental data and the continuous line represents the model.



**Fig. 4.** Comparison of the experimental bubble points [50] of the system CO<sub>2</sub> + HOPMImNO<sub>3</sub> and the isopleths calculated by the GC-EoS. The symbols represent the experimental data and the continuous line represents the model.

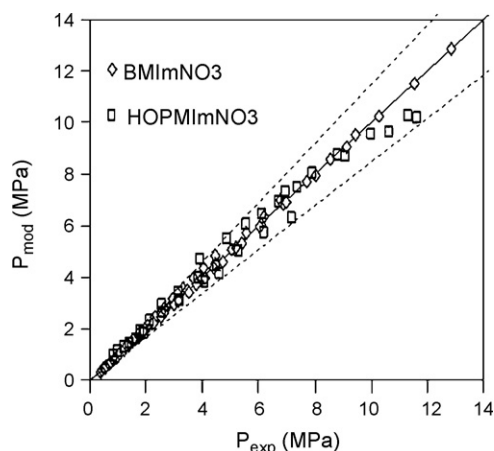


Fig. 5. Parity plot predicted pressure versus experimental pressure. The dotted line indicates a deviation of 15% in pressure.

Table 5

Experimental and calculated infinite dilution activity coefficients for the BMImNO<sub>3</sub> as solvent and several solutes.

Solutes	T (K)	$\gamma_{\text{exp}}^{\infty}$	$\gamma_{\text{calc}}^{\infty}$	% Dev
Hexane	323.15	122.92	105.52	14.16
	363.15	62.52	57.59	7.89
Heptane	323.15	179.22	183.77	2.54
	343.15	110.81	127.21	14.80
	363.15	92.03	92.04	0.01
Ethanol	323.15	0.78	0.70	10.06
	363.15	0.72	0.66	8.15
1-Propanol	323.15	0.96	1.02	5.98
	343.15	0.90	0.95	5.33
	363.15	0.90	0.90	0.00

CO<sub>2</sub> + BMImNO<sub>3</sub> and 6.7% for the system CO<sub>2</sub> + HOPMImNO<sub>3</sub>. Maximum deviation was under 15%, as shown in the parity plot in Fig. 5. The model underpredicted the data of the bubble pressure of the system CO<sub>2</sub> + HOPMImNO<sub>3</sub> at higher pressures. As this did not occur in the CO<sub>2</sub> + BMImNO<sub>3</sub>, where deviations were alike at different pressures, this can be attributed to the non-ideal behavior of the HOPMImNO<sub>3</sub> alcohol group, which is not taken into account by the GC-EoS. The  $\gamma^{\infty}$  were predicted to within an average deviation of 6.9%. The experimental  $\gamma^{\infty}$  are compared to the calculated ones in Table 5.

## 5. Conclusions

Experimental bubble points of the systems CO<sub>2</sub> + HOPMImNO<sub>3</sub> and CO<sub>2</sub> + BMImNO<sub>3</sub>, and experimental values of infinite dilution activity coefficients of the BMImNO<sub>3</sub> in several alkanes and alcohols, were correlated using the GC-EoS. The average error of the calculated bubble points was 2.6% in pressure for the system CO<sub>2</sub> + BMImNO<sub>3</sub> and 6.7% for the system CO<sub>2</sub> + HOPMImNO<sub>3</sub>. The  $\gamma^{\infty}$  could be predicted to within an average deviation of 6.9%.

Group parameters for the group MImNO<sub>3</sub> ( $g^*$  and  $g'$ ) and binary interaction parameters of this group and the functional groups CH<sub>3</sub> ( $k$ ), CH<sub>2</sub> ( $k$ ), CH<sub>2</sub>OH ( $k$ ) and CO<sub>2</sub> ( $k$  and  $\alpha$ ) were fitted. It was necessary to adjust the critical diameter of each IL to achieve a good correlation. Using these parameters, it was possible to calculate equilibrium data of the ILs of the 3-methyl imidazolium nitrate family by fitting only the critical diameter of the considered IL.

## Acknowledgements

M.D.B. thanks the Secretaría de Estado de Universidades e Investigación, Ministerio de Educación y Ciencia (Spain) for financing her postdoctoral grant.

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