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Application of a group contribution equation of state to model the phase behavior of mixtures containing alkanes and ionic liquids

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ABSTRACT

In this work, the group contribution equation of state (GC-EoS) of Skjold-Jørgensen was used to model the phase behavior of mixtures of alkanes with different members of the homologous family 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [*x*-Mpyr][NTf_2] ionic liquids. Pure group parameters for the ionic liquid functional group (MpyrNTf_2) and interaction parameters between this group and the paraffin main group (sub-groups CH_3 and CH_2) were obtained from activity coefficients at infinite dilution found in literature for binary mixture {alkane + [*x*-Mpyr][NTf_2] ionic liquid}. The GC-EoS of Skjold-Jørgensen, extended with these new parameters, was applied to predict with satisfactory results the phase behavior of binary mixtures {alkane + [*x*-Mpyr][NTf_2]}. In order to evaluate the GC-EoS performance in the prediction of liquid–liquid equilibria (LLE), experimental LLE data for binary mixtures {hexane, or heptane, or octane, or nonane, or decane +1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2]} were determined from T = (293.15 to 333.15) K

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1. Introduction

Ionic liquids (ILs) are salts with a melting point below 100 °C, and which are composed entirely by ions. One of the most interesting properties is their very low vapor pressure, which makes them non-polluting substances to the atmosphere. In the last decade, ILs have been studied in numerous fields of science and technology, and presently, their application at industrial level is becoming a real outcome [1,2].

Another important characteristic is the possibility of synthesizing new ILs simply by changing the ions, leading to a very high number of possible ILs which have different properties and can be used in specific applications. However, from the experimental point of view, the determination of the thermophysical properties for all of the synthesized ILs is a highly demanding task in terms of time and costs, becoming in an important limiting factor. For this reason, the development of models and/or empirical equations, which describe satisfactorily the experimental data, is very useful and required. Moreover, these models are an interesting tool to make a preliminary screening of the best ILs, for a specific application.

In the last years, several approaches based on excess Gibbs free energy models, equations of state (EoS), and EoS combined with excess Gibbs free energy models have been applied to provide a successful modeling of experimental data [3]. Among them, those based on EoS are powerful tools, which were used to describe the properties of pure ILs or their mixtures, as well as to model phase behavior of systems containing this kind of compounds [4,5]. As example, the Peng–Robison EoS, was mainly applied to model the solubility of CO_2 in ILs and the vapor liquid equilibrium (VLE) of systems containing ILs and sCO_2, CHF_3 or hydrocarbons [6,7]. This approach was also applied to describe the phase behavior of imidazolium-based ILs and refrigerants [8,9]. The predictive Soave–Redlich–Kwong (PSRK) and cubic plus association (CPA) EoS are other tools used to predict density of pure ILs [10,11] as well as to model the solubility of gases in ILs [5,12–14]. Recently, Hossain and Teja [15] used an extension of the Associated Lattice-Fluid EoS to correlate and predict the volumetric and phase behavior of {CO_2 + imidazolium-based ILs} systems over a wide range of temperature and pressure. Moreover, several variations of the Statitistical Associating Fluid Theory (SAFT) EoS were also used to model the phase behavior of systems with ILs [16–20].

In general, to describe adequately the behavior of this kind of very complex mixtures, these models require an extensive parameterization procedure to obtain the corresponding interaction parameters between the components of the mixture. This procedure can be simplified if molecules are divided into functional groups, as it happens in the group contribution equations of state (GC-EoS) in which intermolecular interactions

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are replaced by group interactions. In fact, the use of group interactions, instead of molecular interactions, is a very useful choice, reducing the number of parameters to be estimated, which also require a less amount of experimental data for the regression

This kind of EoS was already used to describe the phase behavior at high pressures of {gas + ionic liquid} binary mixtures [21–24], obtaining satisfactory results.

In this work, a group-contribution equation of state (GC-EoS) [25,26] was used to represent the thermodynamic behavior of binary mixtures containing alkanes and 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ILs. The properties of the different members of the same family of ILs are calculated by changing the length of the alkyl chain normally attached to the cation; i.e., every ionic liquid is represented by a given cation–anion functional group plus a certain number of alkyl substituents; in this case, the ionic liquid functional group ($MpyrNTf_2$), plus the corresponding CH_3 and CH_2 groups. The same procedure was previously applied to describe the phase behavior at atmospheric pressure of mixtures of hydrocarbons with different members of the homologous family 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [*x*-Mim][NTf_2] [27].

Since a single experimental liquid–liquid equilibrium data point at $T = 298.15$ K was found in the literature [28] for the system {heptane (1) + 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2] (2)}, the LLE data for binary mixtures of alkane (hexane, or heptane, or octane, or nonane, or decane) and the same ionic liquid were experimentally measured from $T = (293.15$ to $333.15)$ K to evaluate the capabilities of the equation of state in the prediction of this phase equilibria.

2. Materials and methods

2.1. Chemicals

The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf_2], was supplied by Iolitec GmbH (Germany) and the hydrocarbons were purchased from different companies. The CAS number, supplier, and purity of each component are summarized in Table 1. Prior to use, the ionic liquid was dried with stirring at moderate temperature ($T = 343.15$ K) and under vacuum ($p = 0.2$ Pa) for at least 48 h. Once dried, its water content was measured with a Mettler Toledo C20Coulometric KF Titrator using Coulomat CG and Coulomat AG, supplied by Sigma–Aldrich, as cathodic and anodic titrants, respectively. The obtained value was 56 ppm. On the other hand, alkanes were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, without any further treatment.

2.2. Experimental LLE

According to the results previously obtained by Pereiro and Rodríguez [28], the ionic liquids were assumed not to be miscible in the hydrocarbon phase in the range of temperatures studied and, therefore, only the solubility of the alkane in the IL-rich phase was determined. To do this, a procedure based on the cloud point method was carried out. Briefly, a known mass of ionic liquid (2 mL approx.) was introduced inside a pre-weighed glass vial of 10 mL, under argon atmosphere, and sealed using a silicon cover. Then, the sample was immersed in a thermostatic bath (Poliscience digital temperature controller, with a stability of ±0.01 K) for at least 1 h. The temperature was controlled using a digital thermometer (ASL model F200) with an uncertainty of ±0.01 K. Once the required temperature was reached, the sample was vigorously stirred while the alkane was very slowly added (drop by drop) on the ionic liquid until turbidity in the mixture was visually observed. Then, the temperature was slightly increased and turbidity disappeared, which confirmed that the cloud point was achieved. At this point, the mixture was weighed again and the composition of the mixture was determined. Before weighing, the vials were carefully dried to avoid weighing errors.

The samples were prepared in triplicate and the mole fractions reported in this work are given as average values. The maximum standard deviation, $\sigma(x)$, was estimated to be 0.010.

Table 1
CAS number, supplier, and purity of the pure components.

Compound	CAS number	Supplier	Purity, in mas fraction
[BMpyr][NTf_2]	223437-11-4	Iolitec	0.99
Hexane	110-54-3	Sigma–Aldrich	0.95
Heptane	142-82-5	VWR	0.997
Octane	111-65-9	Merck	≥0.99
Nonane	111-84-2	Sigma–Aldrich	0.99
Decane	124-18-5	Merck	≥0.99

2.3. Thermodynamic modeling

In this study, pure group parameters for the ionic liquid functional group ($MpyrNTf_2$) and interaction parameters between this group and the paraffin group were obtained from density data of the pure ILs and activity coefficients at infinite dilution in binary mixtures {alkane + [*x*-Mpyr][NTf_2]} found in literature [29–31]. Then, the GC-EoS extended with the obtained parameters was applied to predict the experimental liquid–liquid equilibria (LLE) for binary mixtures {hexane, or heptane, or octane, or nonane, or decane + 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul)imide, [BMpyr][NTf_2]}, and vapor–liquid equilibria (VLE) for binary mixtures {hexane, or octane, or decane (1) +1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul)imide, [HMpyr][NTf_2] (2)} and {hexane, or octane (1) +1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul)imide, [OMpyr][NTf_2] (2)} for which data can be found in the literature [30].

This equation of state combines the generalized van der Waals partition function with the local composition principle. It is written in terms of the residual Helmholtz energy (A^R), as the addition of an attractive term (att) and a free volume (fv) contribution:

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

The Mansoori and Leland expression for hard spheres is used to calculate the free volume term, which takes the following form:

$$\left(\frac{A^R}{RT}\right)_{fv} = 3\left(\frac{\lambda_1\lambda_2}{\lambda_3}\right)(Y-1) + \left(\frac{\lambda_2^3}{\lambda_3^2}\right)(Y^2 - Y - \ln Y) + n\mathrm{Ln}Y \tag{2}$$

$$\lambda_k = \sum_j^{NC} n_j d_j^k \tag{3}$$

$$Y = \left(1 - \frac{\pi\lambda_3}{6V}\right)^{-1} \tag{4}$$

where n, NC, V and d, are the total number of moles, the number of components, the total volume and the hard-sphere diameter per mole, respectively.

The hard-sphere diameter d is considered to be temperature-dependent and is calculated as:

$$d = 1.065655 d_c\left(1 - 0.12\exp\left(\frac{-2T_c}{3T}\right)\right) \tag{5}$$

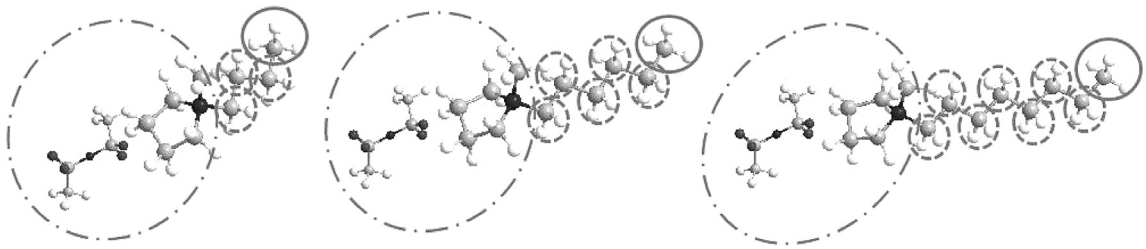

Fig. 1. Decomposition of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul) imide, [BMpyr][NTf_2], 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul) imide, [HMpyr][NTf_2] and 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonul) imide, [OMpyr][NTf_2] ILs into separate functional groups. Groups: (—) CH_3; (– – –) CH_2; (–· –· –) MpyrNTf_2.

where d_c represents the hard-sphere diameter at the critical temperature T_c for the pure component.

The attractive term is a group contribution version of a density dependent NTRL equation [32]:

$$\left(\frac{A^R}{RT}\right)_{att} = -\left(\frac{z}{2}\right)\sum_{i=1}^{NC} n_i \sum_{j=1}^{NG} \upsilon_j^i q_j \sum_{k=1}^{NG} \theta_k \left(\frac{g_{kj}\tilde{q}\tau_{kj}/RTV}{\sum_{l=1}^{NG}\theta_l \tau_{lj}}\right) \tag{6}$$

where

$$\theta_k = \left(\frac{q_k}{\tilde{q}}\right)\sum_{i=1}^{NC} n_i \upsilon_k^i \quad \tilde{q} = \sum_{i=1}^{NC} n_i \sum_{j=1}^{NG} \upsilon_j^i q_j \tag{7}$$

$$\tau_{kj} = \exp\left(\frac{\alpha_{ij}\Delta g_{kj}\tilde{q}}{RTV}\right) \tag{8}$$

$$\Delta g_{kj} = g_{kj} - g_{jj} \tag{9}$$

In Eq. (6), NG is the number of groups, z is the coordination number (set equal to 10); υ_j^i is the number of times group j appears in molecule i; q_j is the number of surface segments assigned to group j; θ_k is the surface fraction of group k; $\tilde{q}$ is the total number of surface segments in the mixture; g_{ij} is the attractive energy parameter for interactions between segments j and i; and α_{ij} is the corresponding nonrandomness parameter. R represents the universal gas constant and T the absolute temperature.

The interactions between unlike segments are defined by:

$$g_{ji} = k_{ji}\sqrt{g_{ii}g_{jj}} \tag{10}$$

where k_{ij} is a binary interaction parameter. For the attractive energy parameter and the binary interaction parameters, their temperature dependences are assumed as:

$$g_{ii} = g_{ii}^*\left[1 + g_{ii}'\left(\frac{T}{T_i^* - 1}\right) + g_{ii}''\ln\left(\frac{T}{T_i^*}\right)\right] \tag{11}$$

$$k_{ij} = k_{ij}^*\left[1 + k_{ij}'\ln\frac{T}{T_{ij}^*}\right] \tag{12}$$

$$T_{ij}^* = 0.5(T_i^* + T_j^*) \tag{13}$$

where T_i^* is the reference temperature for group i.

2.3.1. Ionic liquid functional group

The studied ILs molecules were represented by the (MpyrNTf_2) functional group, plus the corresponding number of CH_2 and CH_3 groups in the side alkyl chain, following the methodology proposed by Breure et al. [22]. Alkanes were represented by the corresponding number of alkyl groups ($2CH_3 + (n-2)$ CH_2 for a C_nH_{n+2}, n-alkane). Representation of [BMpyr][NTf_2], [HMpyr][NTf_2] and [OMpyr][NTf_2] ILs into their corresponding functional groups are plotted in Fig. 1.

2.3.2. Parameterization of the free volume term

The free volume term is characterized by the critical hard-sphere diameter d_c. Usually, critical properties or vapor pressure data of the pure components are used to calculate the critical hard-sphere diameter. However, since ILs have a negligible vapor pressure at normal conditions, this parameter cannot be accurately calculated by this way. Then, an alternative methodology was used to obtain it. The d_c value for the studied ILs was calculated from the van der Waals volumes r_{VdW} using the equation proposed by Espinosa et al. [33] for high molecular weight compounds:

$$\log_{10} d_c = 0.4152 + 0.4128\log_{10} r_{VdW} \tag{14}$$

According to a previous study [27], the van der Waals volumes r_{VdW} for the pure ILs can be estimated from their molar volumes V_m (cm^3/mol), calculated from density data for the pure ILs found in the literature [29,30] (see Table 2). Following this approach, the van der Waals volume of the pure ILs, r_{VdW}, was calculated as:

$$r_{VdW} = 0.04 \times V_m \tag{15}$$

The d_c values obtained with this methodology for [BMpyr][NTf_2], [HMpyr][NTf_2] and [OMpyr][NTf_2] ionic liquids were 7.284 cm/mol, 7.616 cm/mol and 7.917 cm/mol, respectively.

2.3.3. Parameterization of the attractive term

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

- Pure group constants: T_{ii}^*, q_i
- Pure group energy parameters: $g_{ii}^*, g_{ii}' g_{ii}''$
- Group–group interaction parameters: $k^*, k_{ij}', \alpha_{ij}, \alpha_{ji}$

For the CH_3 and CH_2 paraffin sub-groups, the corresponding constants and parameters were taken from the literature [26] (see Tables 3 and 4). As these two sub-groups belong to the same paraffin main group, the interaction parameters between them are zero.

Following the same procedure used and reported in a previous paper for imidazolium-based ILs [27], the surface area q_i of the

Table 2
Density, ρ, molar mass, M_m, and molar volume, V_m, for the pure ionic liquids at T = 298.15 K.

Ionic liquid	ρ/g cm^{-3}	M_m/g mol^{-1}	V_m/cm^3 mol^{-1}	Refs.
[BMpyr][NTf_2]	1.39466	422.41	302.88	[29]
[HMpyr][NTf_2]	1.3353	450.46	337.35	[30]
[OMpyr][NTf_2]	1.2912	478.51	370.59	[30]

Table 3
GC-EoS pure-group parameters.

Group	T^*/K	q	g^*/atm cm^6 mol^{-2}	g'	g''	Source
MpyrNTf$_2$	600	7.434	483993.9	-0.8063	0.0000	This work
CH$_3$	600	0.848	316910.0	-0.9274	0.0000	[26]
CH$_2$	600	0.540	356080.0	-0.8755	0.0000	[26]

Table 4
GC-EoS binary interaction parameters.

i	j	k^*	k'_{ij}	α_{ij}	α_{ji}	Source
MpyrNTf$_2$	CH$_3$	0.7116	−0.0156	4.7519	2.261	This work
MpyrNTf$_2$	CH$_2$	0.7116	−0.0156	4.7519	2.261	This work
CH$_3$	CH$_2$	1.000	0.0000	0.0000	0.0000	[26]

(MpyrNTf$_2$) functional group was estimated from the van der Waals area of the ionic liquid molecule:

$$q_{\mathrm{VdW}} = \frac{z-2}{z} r_{\mathrm{VdW}} + \frac{z}{2} \tag{16}$$

after subtracting the surface area of the side alkyl chain attached to the pyrrolidinium cation. The characteristic temperature T_i^* for the (MpyrNTf$_2$) functional group was fixed at the usual value of 600 K [26].

Pure group energy parameters of (MpyrNTf$_2$) and binary interaction parameters with the paraffin groups were obtained from the correlation of experimental data on infinite dilution activity coefficients of alkanes in 1,1-dialkyl-pyrrolidinium bis (trifluoromethylsulfonyl)imide ILs, found in the literature [30,31]. As can be observed in Table 3, the values for the binary interaction parameters of the (MpyrNTf$_2$) functional group with CH$_3$ and CH$_2$ are the same, because both paraffin sub-groups are members of the same functional main group.

3. Results and discussion

Density, ρ, molar mass, M_m, and molar volume, V_m, data found in the literature for the pure ILs [29,30], measured at T = 298.15 K, are reported in Table 2. These data were used to obtain the critical diameter and the van der Waals area, q, of pure ILs. The q values obtained for pure [BMpyr][NTf$_2$], [HMpyr][NTf$_2$] and [OMpyr][NTf$_2$] ILs were 9.892, 10.995 and 12.059, respectively. From the surface area of each ionic liquid, the q_i value for the ionic liquid functional group (MpyrNTf$_2$) was calculated by subtracting the surface area of the side alkyl chain attached to the pyrrolidinium cation. The q_i value for the (MpyrNTf$_2$) group reported in Table 3 was calculated as an average of the values obtained from each ionic liquid. This value is slightly smaller than that reported by Martín et al. (q_i = 8.032) [23], which was calculated using the method of Bondi [34].

Fig. 2 shows the experimental activity coefficients at infinite dilution used in this work to obtain the energy parameters of the

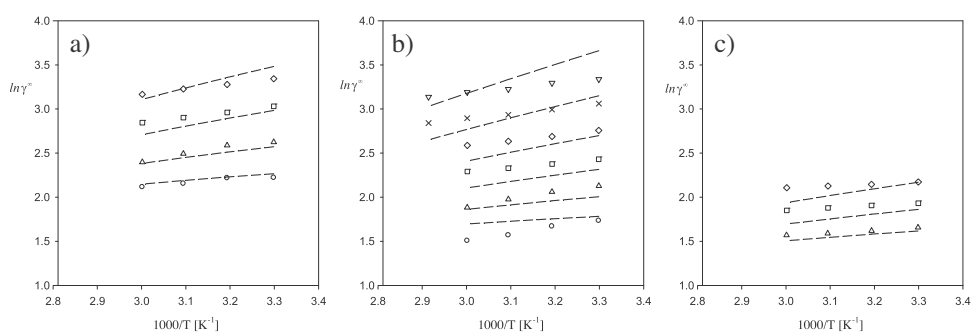

Fig. 2. Activity coefficients at infinite dilution for {alkane (1) +ionic liquid (2)} binary mixtures. Ionic liquids: (a) [BMpyr][NTf$_2$]; (b) [HMpyr][NTf$_2$] and (c) [OMpyr][NTf$_2$]. Dash lines represent GC-EoS prediction and symbols are experimental data taken from literature [30,31]: (○) pentane; (△) hexane; (□) heptane; (◇) octane; (×) nonane; and (▽) decane.

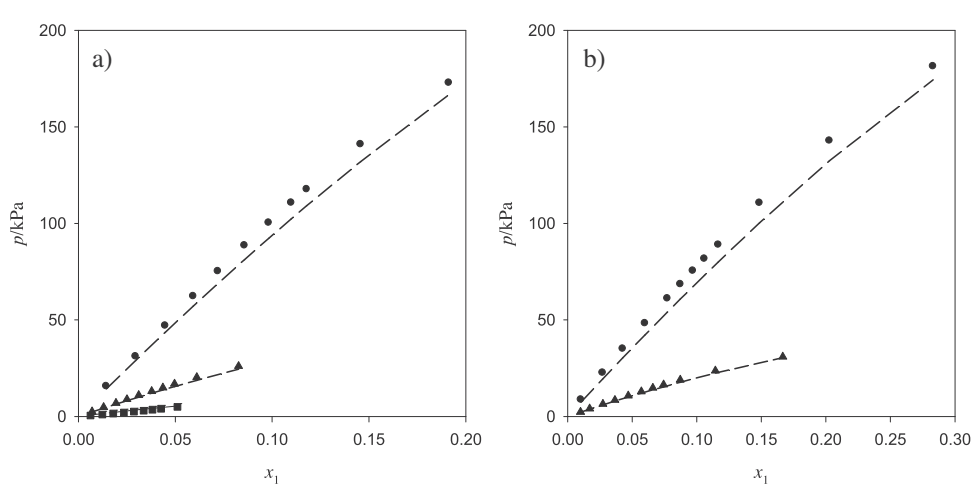

Fig. 3. (a) VLE of the binary system {alkane (1) +[HMpyr][NTf$_2$] (2)} at 363.15 K, and b) VLE of the binary system {alkane (1) +[OMpyr][NTf$_2$] (2)} at 363.15 K. Dash lines show GC-EoS prediction and symbols are experimental data taken from literature [30]: (●) hexane; (▲) octane; and (■) decane.

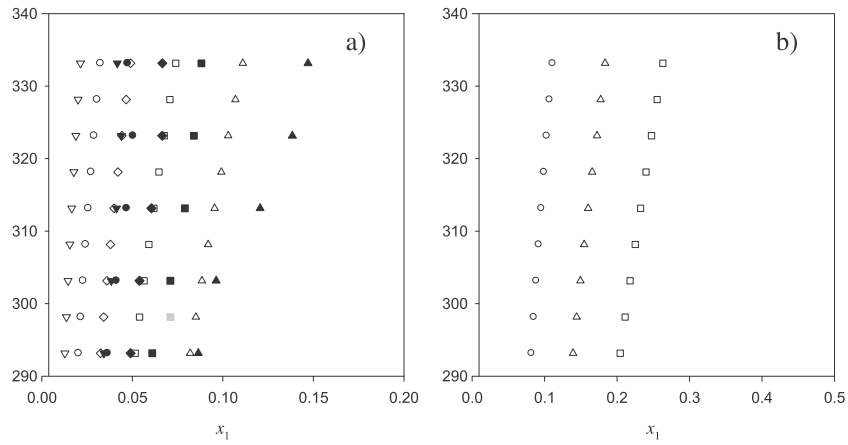

Fig. 4. (a) LLE data for the binary system {alkane (1) +[BMpyr][NTf$_2$] (2)}. Full and empty symbols represent experimental and predicted data, respectively. The gray square is an experimental value taken from literature [28]: (△) hexane; (□) heptane; (◇) octane; (○) nonane; and (▽) decane; (b) Predicted LLE data for the binary system {hexane (1) + ionic liquid (2)}. Symbols: (○) [BMpyr][NTf$_2$]; (△)[HMpyr][NTf$_2$]; (□) [OMpyr][NTf$_2$].

pure group and the binary interaction parameters of (MpyrNTf$_2$) with the paraffin functional groups CH_3 and CH_2. From this figure it is possible to observe that the experimental data were quite well correlated by the GC-EoS equation. The smallest average relative deviation, ARD, was obtained for the mixture {hexane + [OMpyr][NTf$_2$]} (2.21%), while the highest ARD was observed for the system {pentane + BMpyr][NTf$_2$] (13.35%). The ARD was calculated using the following equation:

$$\mathrm{ARD}(\%) = \frac{100}{N} \times \sum_{i=1}^{N} \left| \frac{z_i^{\mathrm{exp}} - z_i^{\mathrm{cal}}}{z_i^{\mathrm{cal}}} \right| \tag{17}$$

where z is the evaluated property (x_1 for LLE, p for VLE, and γ^{∞} for activity coefficients at infinite dilution) and N is the number of data.

In order to confirm the ability of this model to describe the phase behavior of systems containing hydrocarbons and ILs, the GC-EoS equation was applied to predict the vapor–liquid equilibrium (VLE) for the binary mixtures {hexane, or octane, or decane (1) +[HMpyr][NTf$_2$] (2)} and {hexane, or octane (1) +[OMpyr][NTf$_2$] (2)}. The results were compared with experimental data found in the literature [30]. Experimental and predicted VLE data for these systems are plotted together in Fig. 3. As it can be observed, a quite good prediction of the experimental VLE data was achieved with ARD values between 5.97% and 21.67%.

Finally LLE data for binary mixtures {hexane, or heptane, or octane, or nonane, or decane (1) +[BMpyr][NTf$_2$] (2)} and {hexane (1) +[BMpyr][NTf$_2$], or [HMpyr][NTf$_2$], or [OMpyr][NTf$_2$] (2)} were also modeled using the GC-EoS with the parameters reported in this work. Predictions look qualitatively correct. As shown in Fig. 4a, the GC-EoS predicts a quite low solubility of n-alkanes in [BMpyr][NTf$_2$], which decreases as the n-alkane chain length increases. According to Ferreira et al. [35], this trend is independent of both the cation and anion nature of the ILs, and it is associated with the difficulty of the alkanes with a longer chain to fit into the free volume generated by the ionic liquid ions, reducing their packing efficiency. For the systems compared in Fig. 4a, a single experimental LLE datum at T = 298.15 K was found in the literature [28] for the {heptane (1) +[BMpyr][NTf$_2$] (2)} system. In order to validate this model for this type of equilibria, new LLE data for {hexane, or heptane, or octane, or nonane, or decane (1) +[BMpyr][NTf$_2$] (2)} were experimental determined from T = (293.15 to 333.15) K. The obtained results, which are reported in Table 5 and plotted in Fig. 4, confirm that the larger alkanes are less soluble in the ionic liquid, following the same trend predicts by GC-EoS. The experimental data for the binary system with heptane are in the same order of magnitude with that published by Pereiro and Rodríguez [28] obtained at T = 298.15 K. The solubility values predicted by this model are lower than experimental data, and a considerable difference can be observed between the experimental and predicted values. Nevertheless, from a qualitative point of view, the GC-EoS describes quite well the solubility of linear alkanes in [BMpyr][NTf$_2$].

On the other hand, from Fig. 4b it is also possible to observe that GC-EoS predicts that hexane shows a higher solubility in those ILs

Table 5
Experimental LLE data for binary mixture (alkane (1) +[BMpyr][NTf$_2$] (2)) at different temperatures, expressed as mole fraction of alkane, x_1.

x_1	T/K
Hexane + [BMpyr][NTf$_2$]	
0.086	293.15
0.096	303.15
0.121	313.15
0.138	323.15
0.147	333.15
Heptane + [BMpyr][NTf$_2$]	
0.061	293.15
0.071	303.15
0.079	313.15
0.084	323.15
0.088	333.15
Octane + [BMpyr][NTf$_2$]	
0.049	293.15
0.054	303.15
0.061	313.15
0.066	323.15
0.067	333.15
Nonane + [BMpyr][NTf$_2$]	
0.036	293.15
0.041	303.15
0.047	313.15
0.050	323.15
0.047	333.15
Decane + [BMpyr][NTf$_2$]	
0.034	293.15
0.038	303.15
0.041	313.15
0.044	323.15
0.042	333.15

having a longer alkyl chain. That is, this model predicts an increase of the solubility of hexane in the studied ILs with increasing of the alkyl chain length of the cation. This behavior, which has already been observed by several authors, is the result of an increase of free volume and nonpolar region in the ionic liquid, which enhances the accommodation and interaction of alkanes into the ionic liquid [35].

4. Conclusions

In this work, the GC-EoS equation was used to model the phase behavior of mixtures containing ILs of the homologous family of 1-alkyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and alkanes.

Infinite dilution activity coefficients of alkanes in 1,1-dialkyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ILs were used to obtain the energy parameters of the pure ($MpyrNTf_2$) group and its binary interaction parameters with the paraffin functional groups. The GC-EoS extended with these parameters was satisfactorily applied to predict the vapor–liquid equilibria (VLE) for binary mixtures {alkane + 1,1-dialkyl-pyrrolidinium bis(trifluoromethyl-sulfonyl)imide}. From a qualitative point of view, this model is also able to predict the solubility of the alkanes in the [BMpyr][NTf_2], showing a smaller solubility for those alkanes with a longer size. Moreover, this equation of state also predicts that an increase of the ionic liquid alkyl chain leads to an increase of the solubility of hexane in the studied ILs.

The obtained results show that the GC-EoS could be used as a tool to model the phase behavior of this kind of mixtures; although it is not ideal for detailed engineering design, given its simplicity, it is useful for initial screening calculations; it certainly appears accurate on a qualitative basis."

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