MODELING OF HIGH-PRESSURE PHASE EQUILIBRIA OF TERNARY SYSTEMS IONIC LIQUID - ORGANIC - CO$_2$ WITH THE GC-EOS.

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We present in this work the use of the Group Contribution Equation of State to model experimental phase behavior data of ternary mixtures based on an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, bmim[BF$_4$]), carbon dioxide and four different organic solutes. We show that the GC-EOS is able to predict not only L+V→L, but also L$_1$+L$_2$→L phase transitions of ternary systems with good agreement between experimental and predicted values. However, the narrow three-phase region experimentally found has been predicted as consisting of pure CO$_2$, causing the L+V→L$_1$+L$_2$+V and L$_1$+L$_2$+V→L$_1$+L$_2$ phase transitions to be modeled as the vapor-pressure curve of pure CO$_2$. Nevertheless, the deviation with respect to experimental and predicted values for all phase transitions is very satisfactory.

INTRODUCTION

In the last decade, ionic liquids (IL) have emerged as potential candidates for the replacement of common volatile organic solvents in more environmentally friendly industrial processes. Their negligible vapour pressure [1] associated with tuneable physical-chemical properties as a result of the combination of a wide variety of cations and anions [2] makes them very attractive solvents for, among other applications, the performance of reactions and separations. Additionally to these peculiarities, ionic liquids can be associated with carbon dioxide as combined solvents for reactions and extractions. Since the discovery that carbon dioxide is able to tune the miscibility of a mixture ionic liquid + organic [3], several researches have been focused on the application of this phenomenon [4-6]. Nevertheless, in order to profit from the switch in miscibility, knowledge on the phase behaviour of mixtures IL + organic + CO$_2$ is extremely necessary.

In comparison with the large number of studies on ionic liquids, the number of publications on phase behaviour of mixtures is still scarce. This can be justified by the fact that experimental determination of phase transitions is sometimes cumbersome, time-consuming and may involve substances that are toxic, corrosive or harmful to human health or environment. Therefore, there is a clear need for the development of thermodynamic models that allow effective prediction of the phase behaviour of ionic liquid mixtures under CO$_2$ pressure.

Up to now different approaches have been used for modelling the phase behaviour of mixtures with ionic liquids, mostly regarding the solubility of gases. Shariati et al. [7] used the Peng-Robinson Equation of State to model the solubility of fluoroform in the ionic liquid 1-ethyl-3-methylimidazolium hexafluorophosphate, with excellent agreement between

experimental and predicted values. Kato and Gmehling [8] modelled the activity coefficients at infinite dilution for various organic solutes in ionic liquids using original and modified UNIFAC and COSMO-RS equations. The modified UNIFAC equation, which is also based on a group contribution principle, presented satisfactory results for prediction of liquid-vapour equilibrium, excess enthalpies and for the activity coefficients at infinite dilution. The COSMO-RS model showed qualitative agreement with the experimental values. Using a different approach, Kroon et al. [9] showed the capabilities of the tPC-PSAFT equation of state to accurately describe the vapour-liquid equilibrium of IL + CO_2 mixtures taking into account polar interactions between the components. Good correlation was obtained with the tPC-PSAFT, although it was shown that the accuracy of the predictions was dependent on the alkyl-chain length of the IL. Shiflett and Yokozeki modelled the phase behaviour of mixtures of carbon dioxide with ionic liquids of the imidazolium family [10] and trifluoromethane with bmim[PF_6] [11] using the Redlich-Kwong cubic equation of state. The RK-EOS was able to successfully predict not only the high-pressure phase behaviour of these mixtures, but also miscibility gaps for high concentrations of CO_2.

Regarding the modelling of liquid-liquid equilibria, a few articles have been published so far on this subject [12-13]

The Group Contribution Equation of State, GC-EOS, has been already successfully applied in our group for the modelling of solubility of gases in ionic liquids [14, 15]. The GC-EOS has been developed by Skjold-Jorgensen [16] The GC-EOS is based on four main principles and equations in phase equilibrium thermodynamics: the van der Waals partition function; the Carnahan-Starling expression for hard spheres; mixing rules based on an NRTL-like expression for the excess Helmholtz function; and the group contribution principle. This statistical thermodynamics based equation of state is applicable for computation of vapour-liquid and liquid-liquid equilibria of polar as well as non-polar components, over a wide range of temperatures and pressures up to 30 MPa [17]. In this equation, interactions are considered to take place through the surfaces of characteristic groups (segments) rather than through the surfaces of parent molecules. This means that several molecules containing similar groups do not require the estimation of new interaction parameters. Since the number of different ionic liquids that can be synthesized is extremely large, the flexibility of the GC-EOS regarding the division of the ionic liquid molecules into specific groups makes this equation easily applicable to a wide variety of compounds. For additional information on the GC-EOS, the reader is referred elsewhere [14-17].

Since ternary mixtures have been poorly modelled up to now and are of utmost importance for the design of production processes, there is an increase interest in developing equations that can satisfactorily model their complex phase behaviour. Therefore, we extend in this work the use of the GC-EOS for predictions of different phase transitions in mixtures of the type bmim[BF_4] + organic + CO_2. Four different organic compounds, namely acetophenone, 1-phenylethanol, 4-isobutylacetophenone and 1-(4-isobutylphenyl)-ethanol have been selected as organic solutes for the ternary mixtures. Although previously applied for ionic liquids, some binary interaction parameters of the attractive term of the GC-EOS have to be correlated in this work. Nevertheless, excellent agreement has been found for L+V→L phase transitions, and good agreement between experimental and predicted values for L_1+L_2→L phase transitions was found. However, the narrow three-phase region experimentally found has been predicted as consisting of pure CO_2, causing the L+V→L_1+L_2+V and L_1+L_2+V→ L_1+L_2 phase transitions to be modelled as the vapour-pressure curve of pure CO_2. Based on the deviation between calculated and experimental data

points, the GC-EOS can be considered suitable for prediction of phase equilibria in ternary systems based on an ionic liquid and carbon dioxide.

PARAMETERIZATION

The computation of the free volume term in the GC-EOS requires the input of two properties of the pure components: the critical diameter dc and the critical temperature, Tc. The critical temperature is available in literature for most organic compounds; else it is possible to obtain it by estimation methods for critical properties, such as Fedors, Ambrose or Joback. The critical diameter may be obtained from the following equation:

$$d_c = \sqrt[3]{(0.08943 R T_c / P_c)}$$

The values of the critical temperature and critical diameter for the ionic liquid bmim[BF$_4$] were estimated in a previous work by Breure [14, 15] using respectively the Guggenheim equation and the Van der Waals molecular volume of the ionic liquid associated with a correlation developed by Espinosa et al. [18] for saturated alkylesters. However, the values of the critical diameter for three substances investigated in this work were unknown (1-phenylethanol, 4-isobutylacetophenone and 1-(4-isobutylphenyl)-ethanol). Since the vapour-pressure curve and the critical pressure and temperature for these substances were also not available in literature, the critical properties of the solutes were estimated using the Joback method and the dc calculated using the equation shown above. The final values of Tc and dc obtained by this procedure and used in this work are presented in Table 1.

Table 1: Substances investigated in this work and properties used for computation of the free volume term in the GC-EOS model. [a] Obtained from reference [20]

Substance	MW	Tc (K)	dc (cm/mol)
CO$_2$	44.01	304.2	3.1286
bmim[BF$_4$] [14]	226.03	1150	6.5851
acetophenone [19]	120.15	714	5.3776
1-phenylethanol	122.00	699 [a]	5.0179
4-isobutylacetophenone	176.25	772.73	5.8375
1-(4-isobutylphenyl)-ethanol	178.10	792.94	5.8078

The attractive term of the GC-EOS contains not only pure but also binary group parameters. The pure group parameters (gjj*, gjj' and gjj") for the substances involved in this work were collected from literature [14-17]. However, some of the binary interaction parameters (kij*, kij' and αij) between specific groups and the [-mim][BF$_4$] group were not available. Therefore, they were correlated with the GC-EOS in this work, and the values obtained are presented in Table 3. The kij* parameter is assumed to be independent of temperature, therefore kij' values are set equal to zero. Additionally, the non-randomness parameter is considered symmetric, with αij = αji.

Table 2: New GC-EOS binary interaction and non-randomness parameters.

i	j	kij* = kji*	kij'	αij = αji
-mim[BF$_4$]	ACH	0.8078	0	0.1511
-mim[BF$_4$]	AC	0.8078	0	0.1511
-mim[BF$_4$]	CHOH	1.477	0	-0.012
-mim[BF$_4$]	CH3CO	1.3934	0	0.3599

RESULTS AND DISCUSSION

In this work, the GC-EOS has been used to model different phase transitions found experimentally in ternary systems of the type bmim[BF$_4$] + organic + CO$_2$. In total four different ternary systems have been modelled with CO$_2$ compositions below 60 mol%, and one system had CO$_2$ composition higher than 60 mol%, where a more complex phase diagram is found. The necessary parameters for the GC-EOS were found in literature or estimated as described previously. Figure 1 presents the results for the modelling of data with CO$_2$ composition lower than 50 mol%.
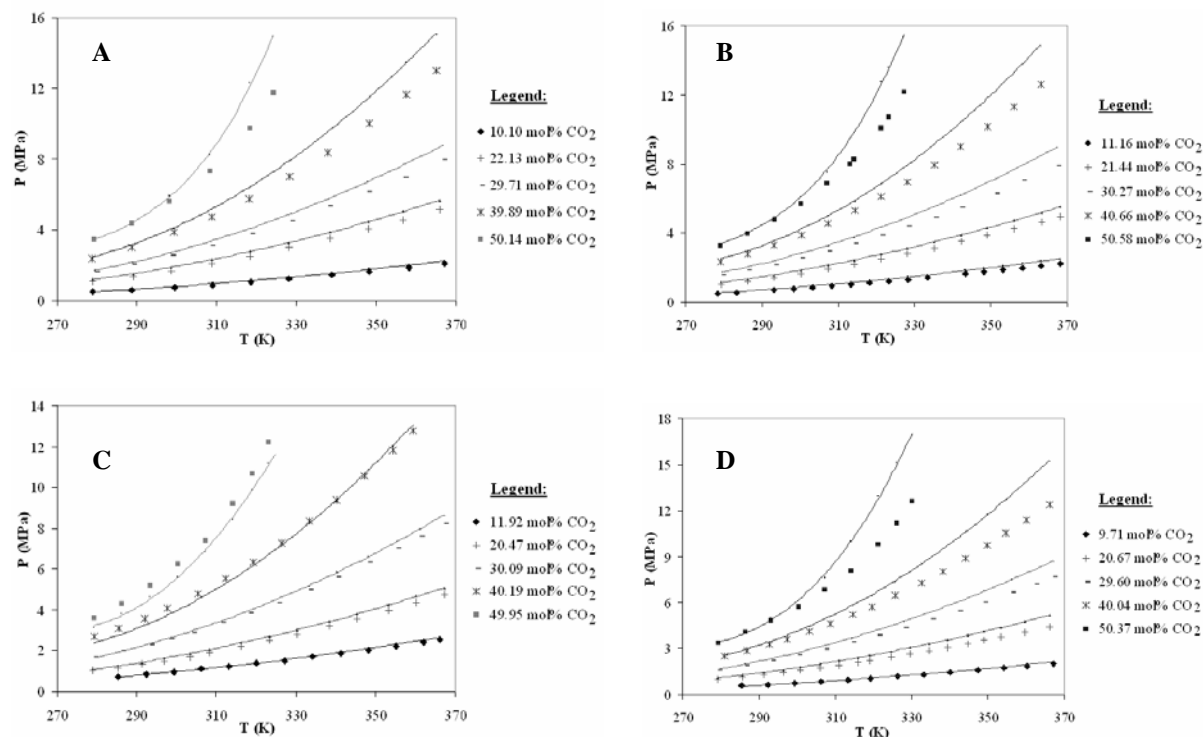
Figure 1: Comparison between model predictions and experimental results for the ternary system: (A) bmim[BF$_4$] + acetophenone + CO$_2$, (B) bmim[BF$_4$] + 4-isobutylacetophenone + CO$_2$, (C) bmim[BF$_4$] + 1-phenylethanol + CO$_2$, (D) bmim[BF$_4$] + 1-(4-isobutylphenyl)-ethanol + CO$_2$.

Figure 1 shows that the GC-EOS model is able to predict the liquid-vapour equilibrium in ternary systems of an ionic liquid, organic solute and carbon dioxide. However, higher CO$_2$ compositions presented higher deviations between calculated and experimental data, which may be caused by a gradual change in molecular structure of the fluid due to intermolecular interactions, e.g. Lewis acid-base interactions between CO$_2$ and the BF$_4^-$ anion, due to an increase in the number of carbon dioxide molecules surrounding solute and the ionic liquid. Additionally, the initial assumption that the parameter kij is independent of temperature (kij'=0) is considered to be one of the reasons why higher deviations were found for predictions at increasing temperatures.

The computational results for different phase-boundaries in the ternary system bmim[BF$_4$] + 4-isobutylacetophenone + CO$_2$ is presented in figure 2.

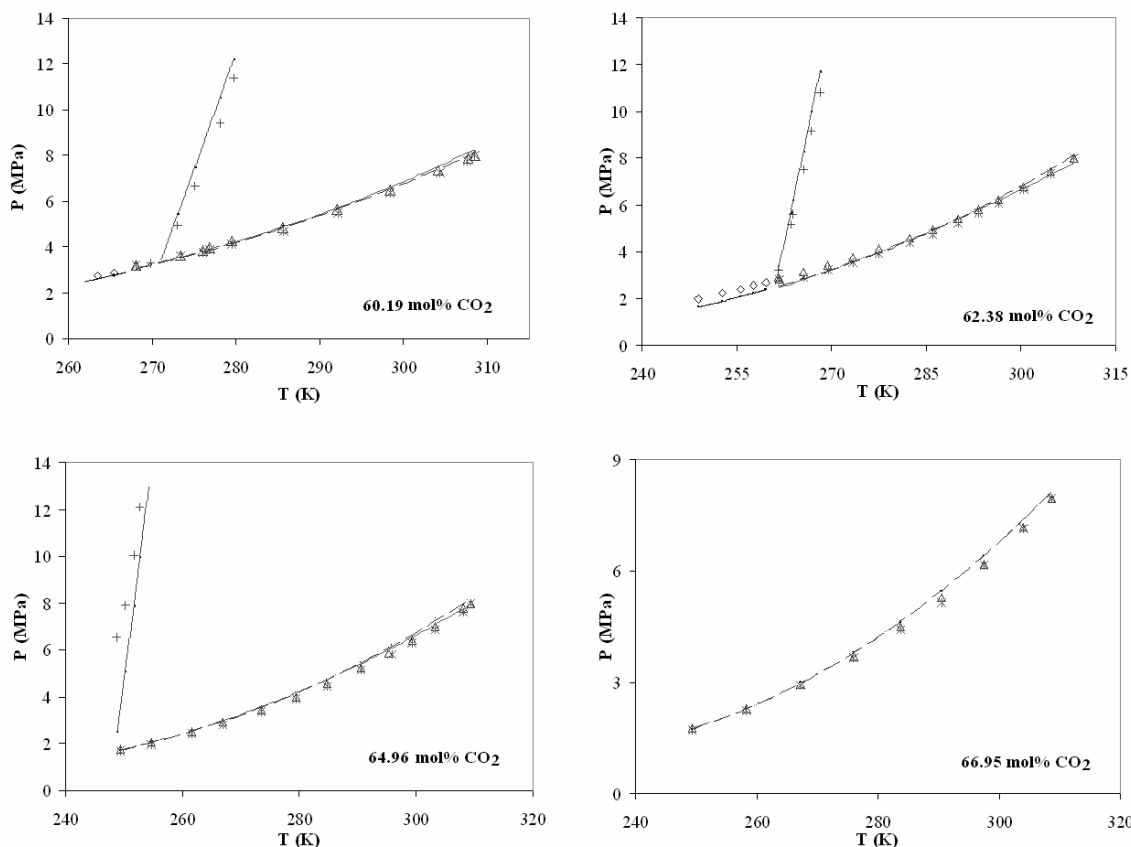**Figure 2:** Comparison between model predictions and experimental results for the ternary system bmim[BF$_4$] + 4-isobutylacetophenone + CO$_2$. Legend for the various phase transitions: open diamonds: L+V→L; crosses: L$_1$+L$_2$→L; stars: L+V→L$_1$+L$_2$+V and open triangles: L$_1$+L$_2$+V→ L$_1$+L$_2$. Lines represent model predictions.

For the more complex phase diagrams as shown in figure 2, the GC-EOS predicted the L+V→L and L$_1$+L$_2$→L equilibria in good agreement with the experimental data. However, the existence of a three-phase region is not accurately predicted for the two systems studied. The very narrow region in which the L$_1$+L$_2$+V three-phase equilibrium is found, is a consequence of the low solubility of the organic solute in carbon dioxide and the absence of ionic liquid in the carbon dioxide phase. Therefore, the intermediary liquid phase (L$_2$) was modelled as pure carbon dioxide i.e., the L+V→ L$_1$+L$_2$+V and L$_1$+L$_2$+V→ L$_1$+L$_2$ phase boundaries were calculated as the pure vapour pressure curve of carbon dioxide. Consequently, the appearance of a second liquid phase can be considered to be the result of partial condensation of carbon dioxide from the vapour phase until complete condensation of the vapour phase is reached and a two-phase L$_1$+L$_2$ equilibrium occurs.

CONCLUSIONS

In this work the applicability of the Group Contribution equation of state has been investigated for modelling the phase behaviour of ternary systems with an ionic liquid, an organic solute and carbon dioxide. The GC-EOS was able to qualitatively describe the liquid-vapour equilibrium for ternary systems with CO$_2$ composition lower than 50 mol%. Improvements in the correlation of experimental data may be achieved by considering the binary parameters kij and gjj as temperature-dependent, and also by taking into account the

asymmetry of the non-randomness parameter αij. Additionally, some modelling inaccuracies may be the result from the fact that the parameters retrieved from literature are estimated in a different temperature region than they are applied in this study.

Since ionic liquids are complex molecules, equations of state models for mixtures with ionic liquids as one of the components that take into account interactions like ionic liquid-solute, ionic liquid-CO_2 and solute-CO_2, can be extremely complicated. Nevertheless, the relatively simple GC-EOS is capable to predict L+V and L_1+L_2 phase equilibria in good agreement with experimental values. Although the three-phase region was not satisfactorily modelled for the two systems studied, the average absolute values for the relative deviation between experimental and predicted values for all different phase transitions which occurred at CO_2 molar fractions higher than 0.60, is about 6%. Therefore, the GC-EOS is considered to be a suitable and relatively simple model to predict phase diagrams for ternary systems with an ionic liquid + organic solute + carbon dioxide.

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