Modeling the Phase Behavior of Ternary Systems Ionic Liquid + Organic + CO_2 with a Group Contribution Equation of State

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This work presents the results of the use of a Group Contribution Equation of State (GC-EOS) to model experimental data obtained for ternary systems of the type bmim[BF_4] + organic solute + CO_2 with four different organic compounds, namely acetophenone, 1-phenylethanol, 4-isobutylacetophenone, and 1-(4-isobutylphenyl)-ethanol. Our results show that the GC-EOS is able to qualitatively predict not only $L+V \rightarrow L$ but also $L_1+L_2 \rightarrow L$ phase transitions. As the two two-phase boundaries $L+V$ and L_1+L_2 of the experimentally found three-phase region L_1+L_2+V almost coincide with the saturated vapor pressure curve of pure CO_2, the phase transitions $L+V \rightarrow L_1+L_2+V$ and $L_1+L_2+V \rightarrow L_1+L_2$ have been represented as this vapor-pressure curve by the model. The average absolute deviations between experimental and predicted values for all phase transitions have been found to be very satisfactory. © 2009 American Institute of Chemical Engineers *AIChE J*, 55: 1265–1273, 2009

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Introduction

In the last decade, ionic liquids (IL) have emerged as potential candidates for the replacement of common volatile

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organic solvents in more environmentally friendly industrial processes. Their negligible vapor pressure[1] associated with tunable 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. As 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, to profit from the switch in miscibility, knowledge on the phase behavior 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 behavior 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 behavior of ionic liquid mixtures under CO_2 pressure.

Up to now different approaches have been used for modeling the phase behavior of mixtures with ionic liquids, mostly regarding the solubility of gases. Shariati and Peters,[7] for instance, 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] modeled 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–vapor 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 vapor-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 modeled the phase behavior 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 behavior of these mixtures, but also miscibility gaps for high concentrations of CO_2. Based on model results, the authors concluded that the system trifluoromethane + bmim[PF_6] behaves as type V fluid mixture, according to the classification of van Konynenburg and Scott.

Regarding the modeling of liquid-liquid equilibria, a few articles have been published so far on this subject. Although developed for non-electrolyte solutions, the NRTL equation described well the liquid-liquid equilibria between IL and organic compounds.[12] The COSMO-RS approach also showed reasonable qualitative agreement between the model predictions and experimental data for different IL + organic mixtures.[13]

Not only equations of state, but also molecular simulations have been used to predict the solubility of gases in ionic liquids. Urukova et al.[14] used Monte-Carlo simulations to predict the solubility of different gases in the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate. The deviations between experimental and predicted results, however, were significantly larger than the results of the previous mentioned studies.

The Group Contribution Equation of State, GC-EOS, has been already successfully applied in our group for the modeling of solubility of gases in ionic liquids.[15] This equation takes into account interactions between specific groups of the molecules, rather than between different molecules themselves. This means that several molecules containing similar groups do not require the estimation of new interaction parameters. Because 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.

As ternary mixtures have been poorly modeled 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 behavior. Therefore, we extend in this work the use of the GC-EOS for predictions of different phase transitions in mixtures of the type IL + organic + CO_2. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate has been selected as the common IL for all ternary systems modeled. 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. Based on the average absolute values for the relative 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.

The GC-EOS Model

The Group Contribution Equation of State, generally referred to as 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 vapor-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

Table 1. Substances Investigated in this Work and Properties used for Computation of the Free Volume Term in the GC-EOS Model

Substance	MW	T_c (K)	d_c (cm/mol)
CO_2	44.01	304.2	3.1286
bmim[BF_4][15]	226.03	1150	6.5851
acetophenone[22]	120.15	714	5.3776
1-phenylethanol	122.00	699*	5.0179†
4-isobutylacetophenone	176.25	772.73‡	5.8375†
1-(4-isobutylphenyl)-ethanol	178.10	792.94‡	5.8078†

*Obtained from reference 23.
‡Estimated with the Joback method.
†Calculated from Eq. 9.

groups (segments) rather than through the surfaces of parent molecules.

For constant temperature, the pressure of a system can be calculated by computation of the Helmholtz energy of the system according to the following relation:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i} \tag{1}$$

The Helmholtz energy is a sum of two parts, one describing the ideal gas (ig) behavior and the second known as residual contribution, which is due to intermolecular forces:

$$A(T,V,n_i) = A^{\text{ig}}(T,V,n_i) + A^{\text{R}}(T,V,n_i) \tag{2}$$

Therefore, the necessary quantities for computation of phase equilibrium can be derived from the expression for the residual Helmholtz function at constant volume, A^{R}, which can be divided into an attractive term (att) and a free volume term (fv):

$$\left(\frac{A^{\text{R}}}{RT}\right)_{T,V,n} = \left(\frac{A^{\text{R}}}{RT}\right)_{\text{fv}} + \left(\frac{A^{\text{R}}}{RT}\right)_{\text{att}} \tag{3}$$

The free volume contribution is assumed to be given by the Carnahan-Starling equation for hard-spheres and is described by the Mansoori and Leland[18] expression for mixtures:

$$\left(\frac{A^{\text{R}}}{RT}\right)_{\text{fv}} = 3(\lambda_1\lambda_2/\lambda_3)(Y-1) + (\lambda_2^3/\lambda_3^2)(Y^2 - Y - \ln Y) + n\ln Y \tag{4}$$

with $\lambda_k = \sum_j^{\text{NC}} n_j d_j^k$ and $Y = (1 - \pi\lambda_3/6V)^{-1}$ where n is the total number of moles, NC the number of components, V the total volume and d the hard-sphere diameter per mole of species, which is temperature-dependant:

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

with d_c being the value of the hard-sphere diameter at the critical temperature T_c for the pure component. The critical diameter can be evaluated by different methodologies, for instance by the vapor pressure data of the component to be considered. The free volume contribution, therefore, contains no binary or higher-order parameters.

The attractive term of the residual Helmholtz function is based on the group contribution concept. The parameters are therefore defined on a segment basis, i.e., the attractive-energy parameter should be the same for a series of molecules containing similar segments. To compensate the total randomness considered in the free volume term, the mixing rules in the attractive term take into account non-randomness. The resulting expression is similar to the NRTL model for the excess Helmholtz function:

$$\left(\frac{A^{\text{R}}}{RT}\right)_{\text{att}} = -(z/2)\sum_i^{\text{NC}} n_i \sum_j^{\text{NG}} v_j^i q_j \sum_k^{\text{NG}} \theta_k (g_{kj}\tilde{q}\tau_{kj}/RTV) \Big/ \sum_i^{\text{NG}} \theta_i \tau_{ij} \tag{6}$$

where $\theta_j = n_j q_j/\tilde{q}$

$$\tilde{q} = \sum_i^{\text{NC}} n_i \sum_j^{\text{NG}} v_j^i q_j$$

$$\Delta g_{ij} = g_{ij} - g_{ii} \quad \text{and} \quad \tau_{ij} = \exp(\alpha_{ij}\Delta g_{ij}\tilde{q}/RTV)$$

where NG is the number of different groups, z is the coordination number, i.e., the number of nearest-neighbor segments to any given segment in a lattice-like structure (which is set to 10), v_j^i is the number of group j in molecule i, q_j is the number of surface segments assigned to group j, θ_k the surface fraction of group k, $\tilde{q}$ the total number of surface segments, g_{ij} the attractive energy parameter for interactions between segments of type j and i, and α_{ij} the corresponding non-randomness parameter, which reflects the deviation from the second-order type of mixing rule used in most simple equations of state.

The interactions between unlike segments are defined by:

Table 2. The Division of the Molecules Studied in this Work into Groups, According to the Group Contribution Principle

	Substances					
Groups	CO_2	bmim[BF_4]	acetophenone	1-phenyl-ethanol	4-isobutyl-acetophenone	1-(4-isobutylphenyl)-ethanol
CO_2	1	0	0	0	0	0
-mim[BF_4]	0	1	0	0	0	0
CH_3	0	1	0	1	2	3
CH_2	0	3	0	0	1	1
CH	0	0	0	0	1	1
ACH	0	0	5	5	4	4
AC*	0	0	1	1	2	2
CHOH	0	0	0	1	0	1
CH_3CO	0	0	1	0	1	0

*A = aromatic.

Table 3. New GC-EOS Binary Interaction and Nonrandomness Parameters

i	j	$k_{ij}^* = k_{ji}'$	k'_{ij}	$\alpha_{ij} = \alpha_{ji}$
-mim[BF_4]	ACH	0.5548	0	0.1977
-mim[BF_4]	AC	0.5548	0	0.1977
-mim[BF_4]	CHOH	2.2153	0	−0.0151
-mim[BF_4]	CH_3CO	1.9084	0	0.0999

$$g_{ji} = k_{ji}\sqrt{g_{ii}g_{jj}} \qquad (k_{ij} = k_{ji}) \tag{7}$$

where k_{ji} is a binary interaction parameter. The following temperature dependences are assumed for the interaction parameters:

$$g_{ii} = g_{ii}^*[1 + g_{ii}'(T/T_i^* - 1) + g_{ii}'' \ln(T/T_i^*)] \quad \text{and}$$

$$k_{ij} = k_{ij}^*[1 + k_{ij}' \ln(T/T_{ij}'')] \tag{8}$$

where $T_{ij}^* = 0.5(T_i^* + T_j^*)$, with T_i* being an arbitrary but fixed reference temperature for group i.

The adjustable parameters of the GC-EOS are g_{jj}*, g_{jj}', g_{jj}'', k_{ij}', k_{ij}' and α_{ij}. The parameters g_{jj}'' and k_{ij}' may often be set to zero and the non-randomness parameters may be neglected for interactions between similar groups, i.e., $\alpha_{ij} = \alpha_{ji} = 0$.[16]

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 d_c and the critical temperature, T_c. 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.[19] The critical diameter may be obtained from Eq. 9:

$$d_c = \sqrt[3]{(0.08943RT_c/P_c)} \tag{9}$$

When the values of T_c and P_c are unknown, estimation of d_c is possible by evaluation of the vapor-pressure curve of the pure component, or by the use of correlations developed for high molecular weight compounds.[20,21] The values of the critical temperature and critical diameter for the ionic liquid bmim[BF_4] were estimated in a previous work by Breure[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.[21] 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). As the vapor-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 d_c calculated using Eq. 9. The final values of T_c and d_c obtained by this procedure are presented in Table 1, together with the substances which ternary systems were modeled in this work with the GC-EOS, and respective values and reference for T_c and d_c.

The attractive term of the GC-EOS contains not only pure but also binary group parameters. For calculation of the

Table 4. Ternary Systems Modeled with the GC-EOS and the Average Absolute Values of the Relative Deviation (AARD) Between Experimental and Calculated Values

System	Number of Experimental Points	AARD (%)
bmim[BF_4]+CO_2[24]	83	6.28
bmim[BF_4]+acetophenone+CO_2[25]	47	20.48
bmim[BF_4]+1-phenylethanol+CO_2[25]	62	10.40
bmim[BF_4]+4-isobutylacetophenone + CO_2 (below 50 mol% CO_2)[26]	70	10.44
bmim[BF_4]+1-(4-isobutylphenyl)-ethanol+CO_2 (below 50 mol% CO_2)[27]	67	11.93
bmim[BF_4]+4-isobutylacetophenone +CO_2 (above 50 mol% CO_2)[28]	146	5.47
bmim[BF_4]+1-(4-isobutylphenyl)-ethanol+CO_2 (above 50 mol% CO_2)[29]	100	5.59

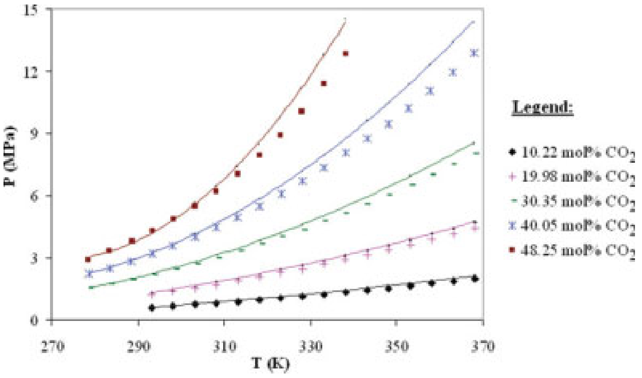

Figure 1. Comparison between experimental (symbols) and modeling (lines) results for the binary system bmim[BF_4] + CO_2.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

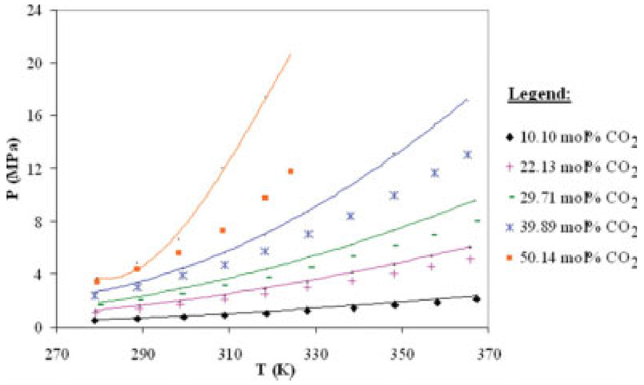

Figure 2. Comparison between model predictions (lines) and experimental results (symbols) for the ternary system bmim[BF_4] + acetophenone + CO_2.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

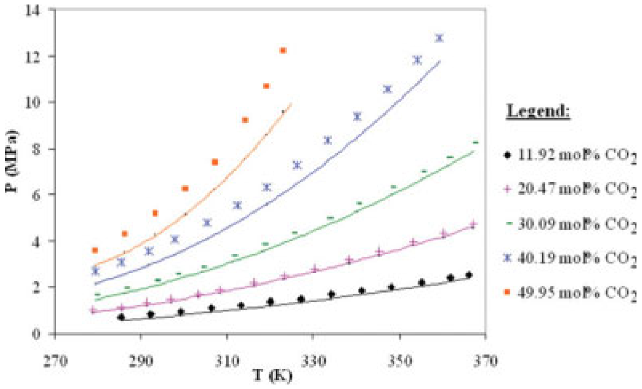

Figure 3. Comparison between model predictions (lines) and experimental results (symbols) for the ternary system bmim[BF$_4$] + 1-phenylethanol + CO$_2$.

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parameters, the molecules of the components of the ternary mixtures were divided in groups, and the contribution of each group to the total value of the parameter is computed. Table 2 presents the assignment of groups for each one of the compounds studied in this work. For more details, the reader is referred elsewhere.[15]

The pure group parameters ($g_{jj}*$, g_{jj}', and g_{jj}'') for the substances involved in this work were collected from literature.[15,17] However, some of the binary interaction parameters ($k_{ij}*$, k_{ij}', and α_{ij}) between specific groups and the [-mim][BF$_4$] group were not available. Therefore, they were correlated with the GC-EOS in this work by using data experimentally obtained for the ternary systems with the solutes 4-isobutylacetophenone and 1-(4-isobutylphenyl)-ethanol and CO$_2$ composition above 50 mol %. From the total number of experimental data points for these two systems (shown in Table 4 as 146 and 100, respectively), 10 to 15

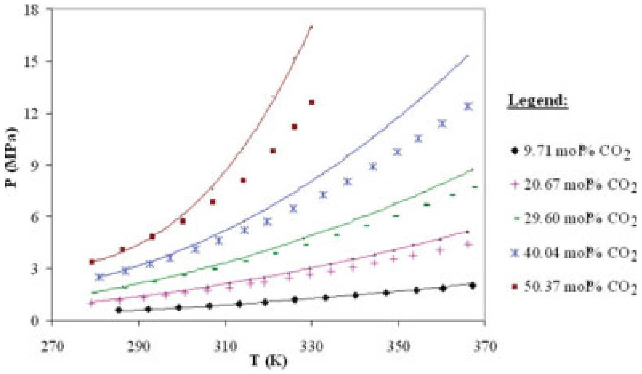

Figure 4. Comparison between model predictions (lines) and experimental results (symbols) for the ternary system bmim[BF$_4$] + 4-isobutylacetophenone + CO$_2$.

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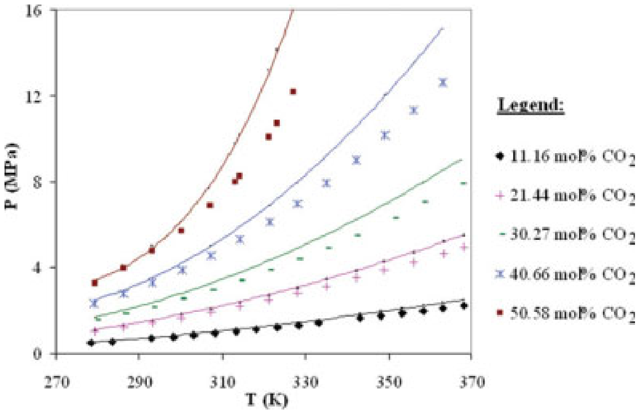

Figure 5. Comparison between model predictions (lines) and experimental results (symbols) for the ternary system bmim[BF$_4$] + 1-(4-isobutylphenyl)-ethanol + CO$_2$.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

points were randomly selected to represent each of the different phase transitions and used to minimize the error between experimental and calculated values when correlating the values of the missing binary interaction parameters. When the error function was minimized to its lowest value, the values of the binary interaction parameters were taken and used for predictions of the other ternary systems. The values of $k_{ij}*$, k_{ij}', and α_{ij} obtained by the above mentioned way are presented in Table 3. The $k_{ij}*$ parameter is assumed to be independent of temperature, therefore k_{ij}' values are set equal to zero. Additionally, the non-randomness parameter is considered symmetric, with $\alpha_{ij} = \alpha_{ji}$.

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 modeled with CO$_2$ compositions below 60 mol %, and two systems 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. Excellent agreement has been found for L+V→L phase transitions, and good agreement between experimental and predicted values for $L_1+L_2 \rightarrow L$ phase transitions was found. However, the narrow three-phase region experimentally found has been predicted as consisting of pure CO$_2$, causing the $L+V \rightarrow L_1+L_2+V$ and $L_1+L_2+V \rightarrow L_1+L_2$ phase transitions to be modeled as the vapor-pressure curve of pure CO$_2$.

Table 4 presents the systems modeled in this work and the average absolute values of the relative deviation (AARD)* between experimental and predicted values.

$^*\mathrm{AARD} = \frac{1}{N_{\exp}} \sum_{i=1}^{N_{\exp}} \left(\frac{|x_{i,\exp} - x_{i,\mathrm{calc}}|}{x_{i,\exp}} \right).$

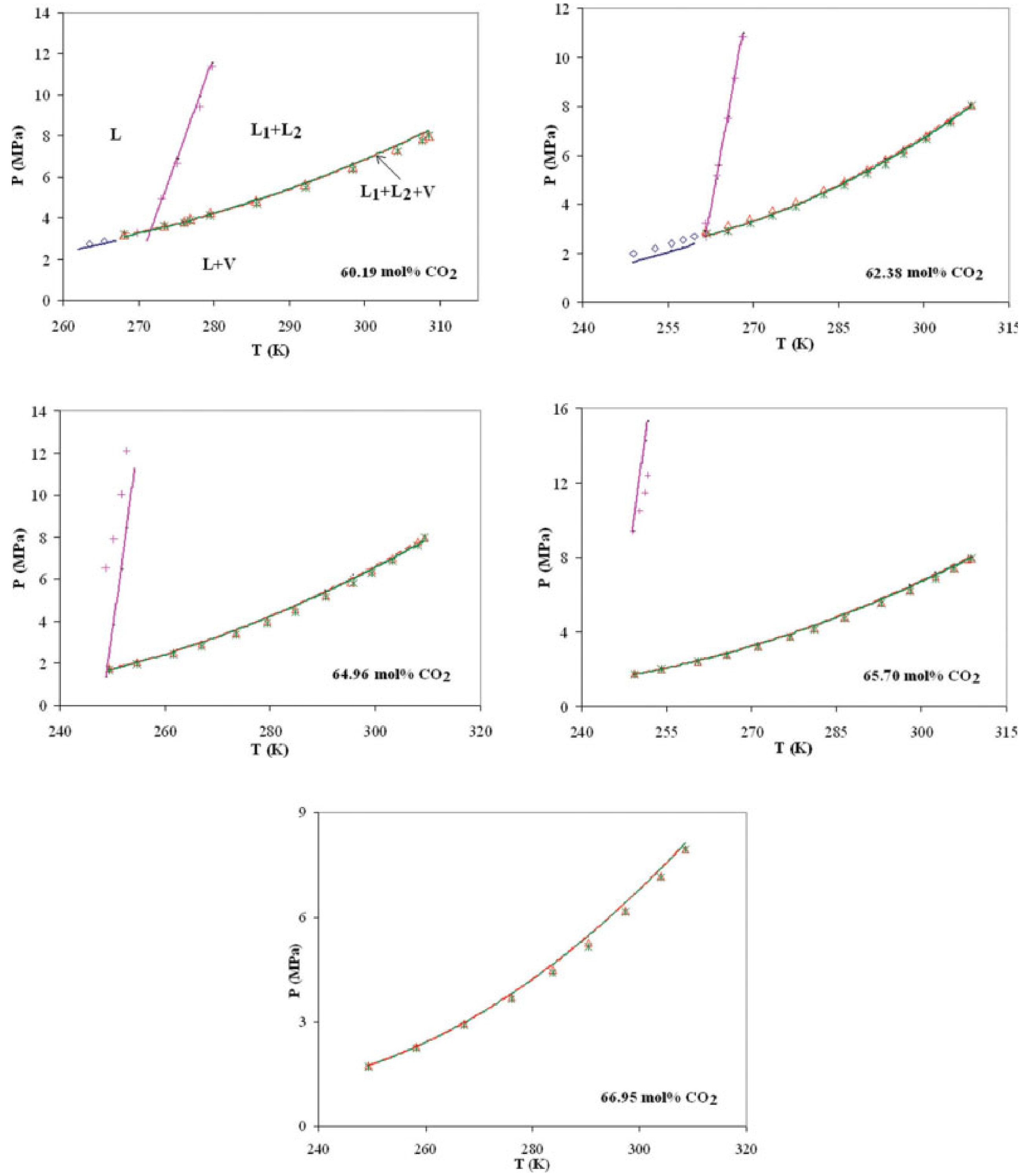

Figure 6. Comparison between model predictions and experimental results for the ternary system bmim[BF_4] + 4-isobutylacetophenone + CO_2.

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. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

From a comparison of the AARD values for the different systems with the expected deviations when the GC-EOS is used (15% according to the work of Skjold-Jorgensen[16,17]), and taking into account the ability of the parameters to predict different phase transitions, the GC-EOS presents acceptable agreement between calculated and experimental values.

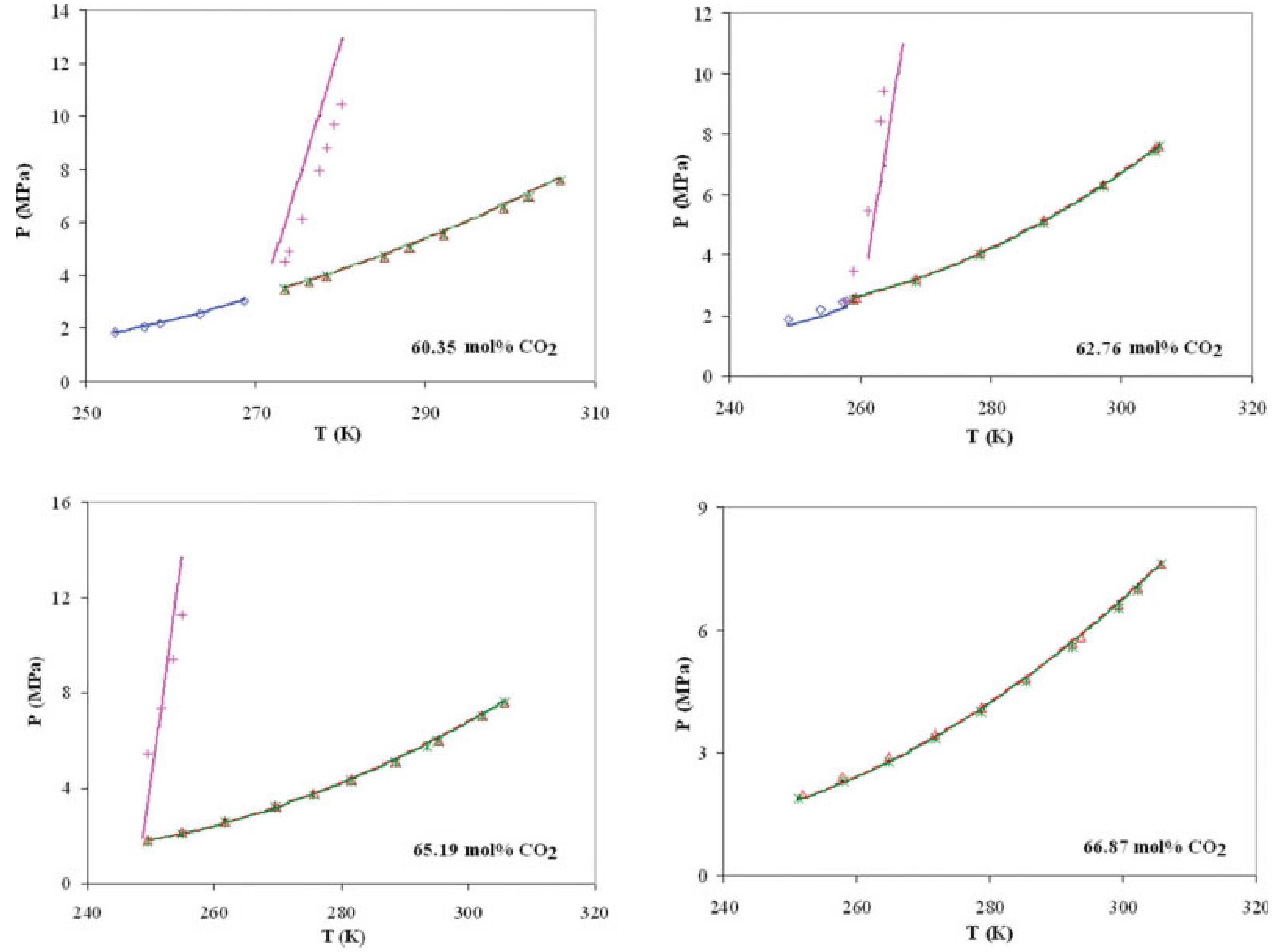

Figure 7. Comparison between model predictions and experimental results for the ternary system bmim[BF$_4$] + 1-(4-isobutylphenyl)-ethanol + CO$_2$.

Legend for phase transitions: open diamonds: L+V→L; crosses: $L_1+L_2 \rightarrow L$; stars: $L+V \rightarrow L_1+L_2+V$ and open triangles: $L_1+L_2+V \rightarrow L_1+L_2$. Lines represent model predictions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figures 1 to 5 present the graphical comparison between experimental data points and the predictions for each one of the systems reported in Table 4 with CO$_2$ compositions lower than 50 mol %, in which only L+V→L phase transitions have been observed.

Figures 1 to 5 show that the GC-EOS model is able to predict the liquid-vapor 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, especially seen in the ternary systems bmim[BF$_4$] + acetophenone + CO$_2$ and bmim[BF$_4$] + 1-phenylethanol + CO$_2$. This effect may be due to a gradual change in molecular structure of the fluid because of intermolecular interactions, e.g. Lewis acid-base interactions between CO$_2$ and the BF$_4^-$ anion, because of an increase in the number of carbon dioxide molecules surrounding solute and the ionic liquid. Additionally, the initial assumption that the parameter k_{ij} is independent of temperature ($k_{ij}' = 0$) 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 systems bmim[BF$_4$] + 4-isobutylacetophenone + CO$_2$ and bmim[BF$_4$] + 1-(4-isobutylphenyl)-ethanol + CO$_2$ are presented in Figures 6 and 7, respectively.

For the more complex phase diagrams as shown in Figures 6 and 7, the GC-EOS predicted the L+V→L and $L_1+L_2 \rightarrow L$ 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, mainly due to the small pressure difference between the two phase boundaries $L_1+L_2+V \rightarrow L_1+L_2$ and $L+V \rightarrow L_1+L_2+V$. 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.[29] Therefore, the intermediary liquid phase (L_2) was modeled as pure carbon dioxide i.e., the $L+V \rightarrow L_1+L_2+V$ and $L_1+L_2+V \rightarrow L_1+L_2$ phase boundaries were calculated as the pure vapor pressure curves 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 vapor phase until complete condensation of the vapor phase is reached and a two-phase L_1+L_2 equilibrium occurs.

To improve the results of the GC-EOS model, some assumptions should be reconsidered. As an example, taking into account the temperature dependence of the binary interaction parameters k_{ij} and g_{jj} may improve the phase equilibrium predictions. Additionally, some modeling 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.

Moreover, the inclusion of an associating term to the GC-EOS[30] that takes into account important molecular interactions such as hydrogen bonds may improve significantly the predictions, especially in mixtures with hydrogen bond donor and/or acceptor compounds, as it is the case in this study.

Conclusions

In this work the applicability of the Group Contribution equation of state has been investigated for modeling the phase behavior of ternary systems with an ionic liquid, an organic solute and carbon dioxide. The GC-EOS was able to qualitatively describe the liquid-vapor 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 parameter k_{ij} as temperature-dependent, and also by taking into account the asymmetry of the non-randomness parameter α_{ij}.

As ionic liquids are complex molecules, equation 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 modeled 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%. Considering the complexity of the experimental data surrounding the three-phase region and the extremely narrow region in which it is found, 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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Notation

A = Helmholtz energy
A^R = residual Helmholtz function
d = hard-sphere diameter
g = interaction parameter
k = binary interaction parameter
n = total number of moles
NC = number of components
NG = number of groups
P = pressure
q = surface parameter
R = gas constant
T = temperature
V = total volume
Y = auxiliary quantity
z = coordination number (z = 10)

Subscripts

att = contribution from attractive forces
c = critical
fv = free volume contribution

Greek letters

α = non-randomness parameter
Δ = difference
θ = surface fraction
λ = auxiliary geometric quantity
v_j^i = number of groups of type j in molecule i
τ = exponential non-randomness weight factor

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