Thermodynamic Modeling of the Phase Behavior of Binary Systems of Ionic Liquids and Carbon Dioxide with the Group Contribution Equation of State

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The group contribution equation of state (GC-EOS) was applied to predict the phase behavior of binary systems of ionic liquids of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO_2. Pure group parameters for the new ionic liquid functional groups [-mim][PF_6] and [-mim][BF_4] and interaction parameters between these groups and the paraffin (CH_3, CH_2) and CO_2 groups were estimated. The GC-EOS extended with the new parameters was applied to predict high-pressure phase equilibria in binary mixtures of the ionic liquids [emim][PF_6], [bmim][PF_6], [hmim][PF_6], [bmim]-[BF_4], [hmim][BF_4], and [omim][BF_4] with CO_2. The agreement between experimental and predicted bubble point data for the ionic liquids was excellent for pressures up to 20 MPa, and even for pressures up to about 100 MPa, the agreement was good. The results show the capability of the GC-EOS to describe phase equilibria of systems consisting of ionic liquids.

Introduction

Over the past decade, room-temperature ionic liquids or simply ionic liquids (ILs) have attracted a great deal of attention as possible replacements for conventional solvents in a number of synthetic processes. ILs are molten organic salts with a melting point below 100 °C. ILs have a couple of features that make them attractive as solvents, including their negligible vapor pressure, their good solubility characteristics, their wide liquid temperature range, and the fact that their physical and chemical properties can be changed through appropriate modifications of the cation, the anion, or the alkyl chains attached to the cation. Numerous chemical reactions have been performed successfully in ILs, including hydrogenations,[1,2] hydroformylations,[2,4] Friedel−Crafts alkylation,[5,6] Diels−Alder reactions,[7,8] and dimerizations.[9,10] However, separation of the products from the reaction medium sometimes exhibits some problems. A promising separation technique for ionic liquids is the extraction of solutes from ionic liquids with supercritical CO_2 ($scCO_2$). Blanchard and Brennecke[11] showed that numerous types of organic compounds, polar and nonpolar, aromatic and aliphatic, volatile and nonvolatile, with a variety of functional groups could all be extracted from the ionic liquid [bmim][PF_6] with $scCO_2$. By employing CO_2 for product recovery, it is possible not only to quantitatively extract the organic solute from the ionic liquid, but also to eliminate the problem of cross-contamination; CO_2 can easily be removed from the ionic liquid by simple depressurization, whereas ionic liquids are not soluble in CO_2, and therefore, no contamination of the products with ionic liquid can take place. In the case of extraction with $scCO_2$, knowledge of the phase behavior of binary systems of ionic liquids and CO_2 is essential for evaluating the viability of the separation process. Considering the large variety of ionic liquids that may be formed, methods to predict the phase behavior of ionic liquids are needed. Up to now, methods to predict the phase behavior of ionic liquids are mostly based on molecular dynamic simulations[12−15] and excess Gibbs models such as NRTL[16−18] and UNIQUAC.[16] In literature, little is mentioned about predicting the phase behavior of systems of ionic liquids using an equation of state approach. Kim et al.[19] used a group contribution nonrandom lattice-fluid equation of state to predict solubilities of CO_2 in the ionic liquids [hmim][PF_6], [emim]-[BF_4], [hmim][BF_4], [emim][Tf_2N], and [hmim][Tf_2N] at pressures up to 1 MPa. For the ionic liquid [bmim][PF_6], predictions were made for pressures up to 10 MPa. The agreements between experimental and calculated solubilities were generally good. However, no information was available for higher pressures (>1 MPa). Shariati and Peters[20] used a Peng−Robinson equation of state to model the high-pressure phase behavior of the system fluoroform and [emim][PF_6]. They showed that the Peng−Robinson equation of state is capable of describing the experimental bubble points of this system and to qualitatively predict the solubility of the ionic liquids in supercritical fluoroform. Recently, Kroon et al.[21] presented a modified PC-SAFT equation to model binary systems of CO_2 and certain ionic liquids. In the present study, it is examined if the group contribution equation of state (GC-EOS) is capable of predicting the phase behavior of binary systems of ionic liquids of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO_2.

GC-EOS Model

In this work, the GC-EOS equation is used to model binary systems of ionic liquids and CO_2. The GC-EOS was developed in the 1980s by Skjold-Jørgensen[22,23] to calculate vapor−liquid

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equilibria of nonideal mixtures up to pressures of 30 MPa. The basis of the GC-EOS is the generalized van der Waals function combined with the local composition principle. In terms of the residual Helmholtz energy:

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

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

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

with

$$\lambda_k = \sum_j^{NC} n_j d_j^k \text{ and } Y = (1 - \pi\lambda_3/6V)^{-1}$$

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 temperature-dependent and is described by the following generalized expression:

$$d = 1.065655 d_c(1 - 0.12 \exp(-2T_c/3T)) \quad (3)$$

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:

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

where

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

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

In eq 4, z is the number of nearest neighbors to any segment (set equal 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 is the surface fraction of group k; $\tilde{q}$ is the total number of surface segments; g_{ij} is the attractive energy parameter for interactions between segments j and i; and α_{ij} is the corresponding nonrandomness parameter.

The interactions between unlike segments are defined by:

$$g_{ji} = k_{ji}\sqrt{g_{ii}g_{jj}} \quad (5)$$

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

$$g_{ii} = g_{ii}^*[1 + g_{ii}'(T/T_i^* - 1) + g_{ii}'' \ln(T/T_i^*)] \quad (6)$$

and

$$k_{ij} = k_{ij}^*[1 + k_{ij}' \ln(T/T_{ij}^*)] \quad (7)$$

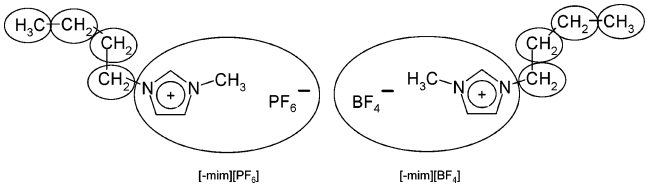

Figure 1. Decomposition of the ionic liquids [bmim][PF_6] (left) and [bmim][BF_4] (right) into separate functional groups.

where

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

T_i^* is an arbitrary but fixed reference temperature for group i.

Thermodynamic Modeling

In this work, the capability of the GC-EOS to represent the phase behavior of mixtures of ionic liquids of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO_2 is studied. Pure group and binary interaction parameters for the new functional groups [-mim]-[PF_6] and [-mim][BF_4] are estimated on the basis of experimental information for the ionic liquids [hmim][PF_6] and [hmim][BF_4]. The GC-EOS extended with the new parameters is then used to predict the phase behavior of binary systems of the ionic liquids [emim][PF_6], [bmim][PF_6], [bmim][BF_4], and [omim][BF_4] and CO_2.

Ionic Liquid Functional Groups. The ionic liquids of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate were decomposed into separate functional groups as shown in Figure 1. As an example, [bmim]-[PF_6] is decomposed into one CH_3 group, three CH_2 groups, and a functional group consisting of the methylimidazolium cation and hexafluorophoshate anion, further referred to as the [-mim][PF_6] group.

Ionic liquids of the homologous family 1-alkyl-3-methylimidazolium tetrafluoroborate were decomposed in a similar way, namely, into a CH_3 group, various CH_2 groups (depending on the length of the alkyl chain), and a group consisting of the methylimidazolium cation and the tetrafluoroborate anion [-mim][BF_4].

Parametrization 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 normally calculated from critical properties or by fitting the equation to a vapor pressure data point (generally the normal boiling point). Since the main characteristic of ionic liquids is their negligible vapor pressure, this type of information is not available for ionic liquids. Espinosa et al.[24,25] have developed a correlation between the critical diameter d_c and the normalized van der Waals molecular volume (r) of high molecular weight compounds (n-alkanes, n-alkenes, saturated and unsaturated triacylglycerides, and alkylesters). This correlation was applied to calculate the critical diameter of ionic liquids from the estimated van der Waals volumes.

Following a group-contribution approach, the normalized van der Waals volume of a compound can be calculated as the sum of the constituent group volume parameters R_k:

$$r_i = \sum_{k=1} \nu_k^{(i)} R_k$$

where $\nu_k^{(i)}$ is the number of groups k in molecule i.

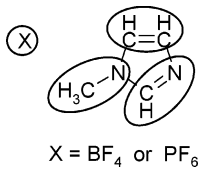

Figure 2. Units contained in the [-mim][PF_6] and [-mim][PF_6] functional groups.

TABLE 1: Group Volume (R_k) and Surface Area (Q_k) Parameters Used in This Work

group or unit	R_k	Q_k	source
CH_3	0.9011	0.848	Bondi [28]
CH_2	0.6744	0.540	Bondi [28]
[-mim][PF_6]	4.179	4.098	Calculated from *a,b,c,d,e*
[-mim][BF_4]	6.5494	5.983	Calculated from *a,b,c,e,f*
CH═CH[a]	1.1167	0.867	Bondi [28]
CH3−N[b]	1.1865	0.940	Bondi [28]
CH═N[c]	0.7329	0.324	Bondi [28]
P[d]	1.1404	1.092	DIPPR databank [40]
F[e]	0.3955	0.460	Bondi [28]
BF_3[f]	1.7474	1.507	DIPPR databank [40]

TABLE 2: Values for d_c and T_c Used in This Work

ionic liquid	r	d_c (cm/mol)	T_c (K)
[emim][PF_6]	8.125	6.177	1150
[bmim][PF_6]	9.474	6.581	1100
[hmim][PF_6]	10.823	6.953	1050
[bmim][BF_4]	8.103	6.585	1150
[hmim][BF_4]	9.452	6.989	1100
[omim][BF_4]	10.801	7.360	1050

TABLE 3: Parameters in the Attractive Term of the GC-EOS

pure group constants	T_i^*, q_i
pure group energy parameters	g_{ii}^*, g_{ii}', g_{ii}''
group−group interaction parameters	k_{ij}^*, k_{ij}', α_{ij}, α_{ji}

Similarly, the number of surface segments assigned to molecule *i* can be calculated from the corresponding values of the functional groups:

$$q_i = \sum_{k=1} \nu_k^{(i)} Q_k$$

The group parameters R_k and Q_k represent the van der Waals volume and surface area, normalized by a standard segment volume of 15.17×10^{-6} m^3/mol and segment area of 2.5×10^5 m^2/mol, as in the UNIFAC model.[39]

The volume R_k and area Q_k parameters of [-mim][PF_6] and [-mim][BF_4] functional groups were calculated from the constituents units shown in Figure 2. Table 1 contains the values of R_k and Q_k of units and functional groups, calculated from the van der Waals volumes and surface areas given by Bondi[28] or reported in the DIPPR data bank.

The calculated normalized van der Waals volume and critical diameter of the ionic liquids studied in this work are reported in Table 2.

In order to calculate the temperature-dependent hard sphere diameter from eq 3, a value of the critical temperature is required. Rebelo et al.[26] estimated critical temperatures for various ionic liquids based on experimental surface tension and density data. The values of the critical temperatures for the ionic liquids used in this work are also reported in Table 2.

Parametrization of the Attractive Term. Table 3 shows the parameters required to calculate the attractive term of the GC-EOS. Pure group and binary interaction parameters for many gases and solvent groups have been reported in literature. Pure group parameters for the functional groups CH_3, CH_2, and CO_2 were taken from Skjold-Jørgensen.[22,23] Binary parameters for interactions between CO_2 and the paraffin groups were taken from Espinosa et al.[27] In this work, pure group parameters were determined for the functional groups [-mim][PF_6] and [-mim][BF_4], and binary interaction parameters were obtained for interactions between these groups and the functional groups CH_3, CH_2, and CO_2. Following Skjold-Jørgensen's original procedure,[22] the characteristic temperature T^* of the [-mim][PF_6] and [-mim][BF_4] groups was set equal to 600 K.

TABLE 4: New GC-EOS Parameters

	pure group parameters				
group	T^* (K)	q	g^*	g'	g''
[-mim][PF_6]	600	4.891	954500	−0.5931	0.0
[-mim][BF_4]	600	4.098	1013000	−1.5857	0.0

	binary interaction parameters				
I	j	k_{ij}^*	k_{ij}'	α_{ij}	α_{ji}
[-mim][PF_{6-}]	CH_3	0.871	0.0	−3.826	−0.857
[-mim][PF_6]	CH_2	0.871	0.0	−3.826	−0.857
[-mim][PF_6]	CO_2	0.885	0.0	−5.656	0.833
[-mim][BF_4]	CH_3	0.791	0.0	−1.002	−1.001
[-mim][BF_4]	CH_2	0.791	0.0	−1.002	−1.001
[-mim][BF_4]	CO_2	0.601	0.0	0.471	11.068

The attractive energy parameter (g_{ii}) for the [-mim][PF_6] and [-mim][BF_4] groups and the binary interaction parameters (k_{ij} and α_{ij}) between [-mim][PF_6] and [-mim][BF-$_4$] and the paraffin (CH_2 and CH_3) functional groups were calculated by fitting infinite dilution activity coefficients of alkanes in the ionic liquids [hmim][PF_6][29] and [hmim][BF_4],[30] respectively. In order to find the optimal set of parameters for a given set of input data, the following objective function was minimized.

$$F = \sum_{i=1}^{N-\text{data}} [(\gamma_{i,\text{alkane,calc}}^{\infty}/\gamma_{i,\text{alkane,expt}}^{\infty} - 1.0)^2]$$

The binary interaction parameters (k_{ij} and α_{ij}) between CO_2 and the [-mim][PF_6] and [-mim]BF_4] groups were obtained by fitting bubble point data of CO_2 in the ionic liquid [hmim][PF_6][33] and [hmim][BF_4],[36] respectively. The most suitable set of parameters for a given set of input data were those that satisfied the isofugacity criteria, according to the following objective function:

$$F = \sum_{i=1}^{N-\text{data}} [(x_{i,\text{CO}_2,\text{exp}} \varphi_{i,\text{CO}_2}^{L(T,P,x)_{\text{exp}}} / y_{i,\text{CO}_2,\text{exp}} \varphi_{i,\text{CO}_2}^{V(T,P,y)_{\text{exp}}} - 1)^2]$$

Since ionic liquids have a negligible vapor pressure (i.e., $y_{IL} \sim 0$) the objective function F_φ was solved for carbon dioxide only.

In order to keep the number of parameters as low as possible, and if there was no significant improvement in reproducing experimental data, the following fitting strategy was adopted:

(a) A linear temperature dependence was assumed for the attractive energy parameter g_{ii} (i.e., $g_{ii}'' = 0$).

(b) The same values were given to the binary interaction parameters of both paraffin groups CH_3 and CH_2, since they are members of the same family of functional groups.

(c) The k_{ij} binary interaction parameter is temperature-independent (i.e. $k_{ij}' = 0$)

The new pure group and interaction parameters estimated in this work are given in Table 4.

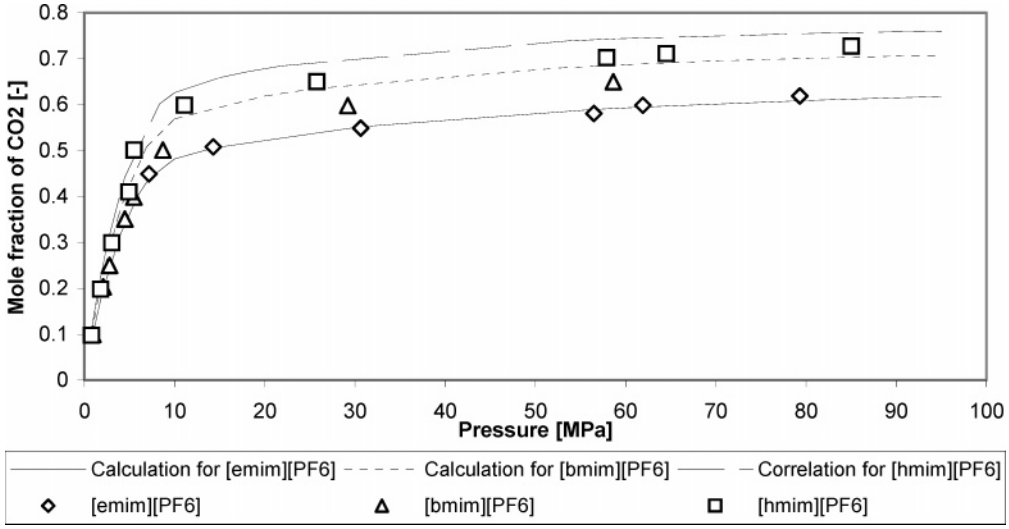

Figure 3. Comparison between GC-EOS calculations and experimental bubble point data for binary systems of the ionic liquids [emim][PF_6], [bmim][PF_6], and [hmim][PF_6] with CO_2 at 313 K.

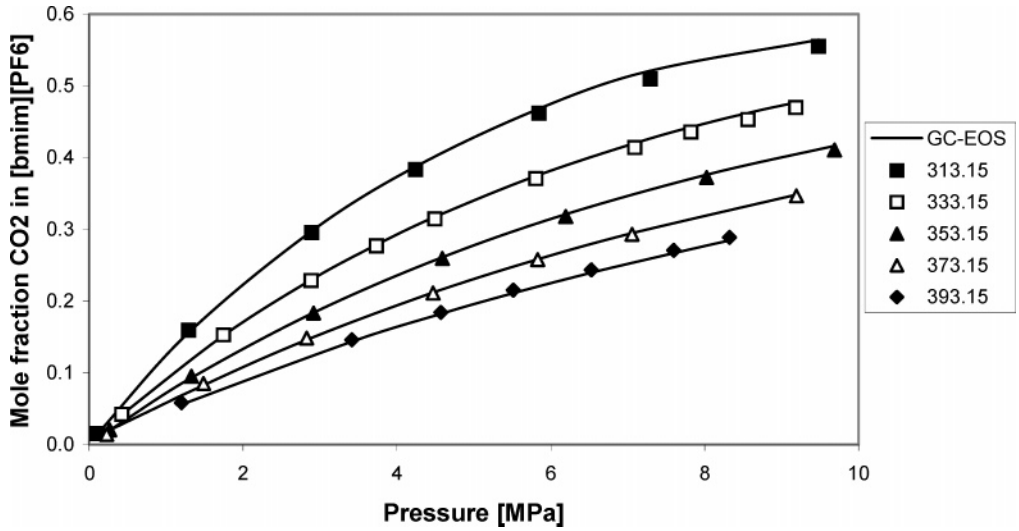

Figure 4. Comparison of experimental bubble point data[31] with predicted values for binary systems of [bmim][PF_6] and CO_2.

Results and Discussion

The GC-EOS extended with new parameters reported in Table 4, found by fitting experimental data for the ionic liquids [hmim]-[PF_6] and [hmim][BF_4], was used to predict the phase behavior of systems of CO_2 with the ionic liquids [emim][PF_6], [bmim]-[PF_6], [bmim][BF_4], and [omim][BF_4]. In Figure 3, results are shown for the ionic liquids [emim][PF_6], [bmim][PF_6], and [hmim][PF_6] at 313 K. In Figure 4, GC-EOS predictions are compared with the experimental data of Kamps et al.[31] for the ionic liquid [bmim][PF_6]. The GC-EOS model is able to accurately describe the phase behavior of the binary system [emim][PF_6] + CO_2 up to pressures of about 100 MPa. For the binary system [bmim][PF_6] + CO_2, predictions are excellent for pressures up to 10 MPa and for temperatures varying between 293.15 and 393.15 K (see Figure 4). At higher pressures, deviations between predicted and experimental values become larger (see Figure 3). Also, for the ionic liquid [hmim]-[PF_6], the deviations between experimental and correlated values are larger at higher pressures. For both, [bmim][PF_6] and [hmim]-[PF_6], the GC-EOS predicts that the solubility of CO_2 at elevated pressures is higher than is measured experimentally.

In Figure 5, GC-EOS predictions are compared with experimental data for the ionic liquids [bmim][BF_4], [hmim][BF_4], and [omim][BF_4] at 313 K. For the ionic liquid [bmim][BF_4], deviations between experimental and calculated values are higher at low CO_2 concentrations and decrease with increasing pressure. The correlations for [hmim][BF_4] and the predictions for [omim][BF_4] are very good over the whole pressure range.

Characteristic of the phase behavior of systems of ionic liquids and CO_2 is that, at low concentrations of CO_2, the equilibrium pressure of the system is very low. When the CO_2 concentration is increased isothermally, the equilibrium pressure increases steeply. The GC-EOS is capable of describing this characteristic phase behavior of ionic liquids.

Comparisons between experimental data and GC-EOS predictions are summarized in Table 5. From this table, it becomes clear that the agreement between experimental and predicted data is very good even up to pressures of about 100 MPa.

The GC-EOS can also be used to predict the composition of the dew points at a certain temperature and pressure. In literature, little is reported about the solubility of ionic liquids in a CO_2-rich phase. However, it is expected that the solubility of ionic liquids in CO_2 is extremely low as a result of their negligible vapor pressure and the fact that nonpolar CO_2 is not capable of solvating ions. Blanchard et al.[37] performed extraction experiments with CO_2 in the ionic liquid [bmim][PF_6]. They found

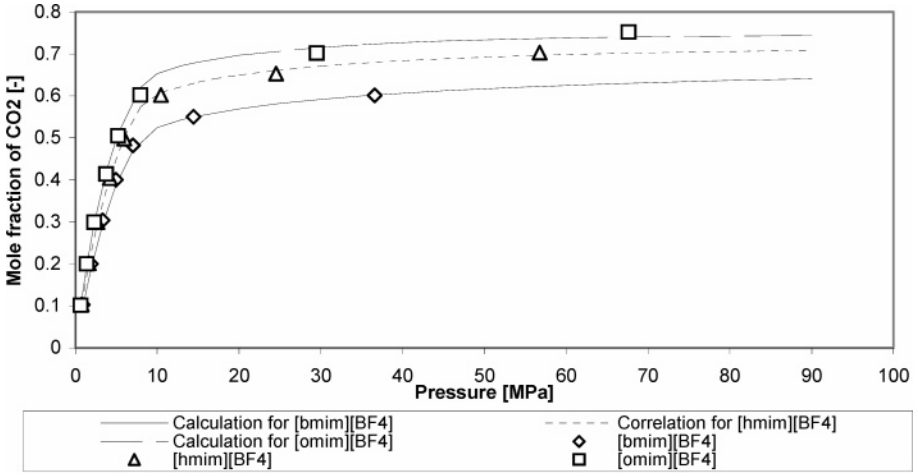

Figure 5. Comparison between GC-EOS calculations and experimental bubble point data for binary systems of the ionic liquids [bmim][BF_4], [hmim][BF_4], and [omim][BF_4] with CO_2 at 313 K.

TABLE 5: Comparison of Experimental Data with Calculated Results Obtained with the GC-EOS Model

ionic liquid	*T* range [K]	*P* range [K]	no. of data points	AAD [%]	ref
[emim][PF_6]	308.14 366.03	1.49−97.10	74	1.76	[32]
[bmim][PF_6]	293.15−393.15	0.105−9.685	43	2.26	[31]
[bmim][PF_6]	293.29−363.54	0.59−73.50	99	1.72	[34]
[hmim][PF_6]	298.31−363.58	0.64−94.60	98	2.83	[33]
[hmim][PF_6]	298.15	0.296−0.927	14	1.75	[19]
[bmim][BF_4]	278.47−367.92	0.587−67.62	104	3.67	[35]
[hmim][BF_4]	293.18−368.16	0.54−86.60	104	0.94	[36]
[omim][BF_4]	308.20−363.29	0.57−85.80	100	1.37	

TABLE 6: Comparison of Experimental Solubilities of [bmim][PF_6][38] in CO_2 with GC-EOS Predictions

T [°C]	*P* [MPa]	$y_{[bmim][PF6]}$ exptl [-]	$y_{[bmim][PF6]}$ calcd [-]
40	12	1.8×10^{-7}	5.88×10^{-5}
40	15	3.2×10^{-7}	1.22×10^{-4}
55	15	1.4×10^{-7}	5.32×10^{-5}

that at 40 °C and 13.8 MPa there was no detectable [bmim]-[PF_6] in the extract, indicating that the solubility in CO_2 is less that 10^{-5} mole fraction. Wu et al.[38] measured the solubility of [bmim][PF_6] in scCO_2 at various temperatures and pressures. In Table 6, these experimental solubilities are compared with the GC-EOS predictions.

According to Table 6, the GC-EOS predicts that the solubility of [bmim][PF_6] in CO_2 is higher than that which is measured experimentally. This can be attributed to the fact that the present GC-EOS extended with the new parameters does not take into account that ionic liquids consist of separate ions and that CO_2 is less capable of solvating ions. Instead, the GC-EOS regards ionic liquids as low volatile compounds, and the solubility of ionic liquids in carbon dioxide shows a similar dependence on pressure and temperature.

Conclusions

The GC-EOS equation was used to model the phase behavior of mixtures of ionic liquids of the homologous families 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO_2. For this purpose, two new functional groups were defined, consisting of the methylimidazolium cation and the hexafluorophosphate or tetrafluoroborate anion, referred to as the functional groups [-mim][PF_6] and [-mim][BF_4], respectively. The parameter table for the GC-EOS has been extended to include pure group parameters for the [-mim][PF_6] and [-mim]-[BF_4] ionic liquid groups and binary parameters for interactions between these and functional groups CH_3, CH_2, and CO_2. The GC-EOS extended with these parameters is capable of predicting the phase behavior of binary systems of the ionic liquids [emim]-[PF_6], [bmim][PF_6], [hmim][PF_6], [bmim][BF_4], [hmim][BF_4], and [omim][BF_4] with CO_2. The agreement between predicted and experimental values is very good for pressures up to 20 MPa, and even for pressures up to 100 MPa, good results were obtained. The results show the capability of the GC-EOS model to describe the phase behavior of binary systems of ionic liquids and CO_2 and its potential for modeling supercritical processes involving ionic liquids.

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