

## GENERAL RESEARCH

## Irregular Ionic Lattice Model for Gas Solubilities in Ionic Liquids

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The irregular ionic lattice model (IILM) is applied to predict the vapor pressures and solubilities of carbon dioxide dissolved in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) and in 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C8mim][BF<sub>4</sub>]) ionic liquids at temperatures ranging from 298.15 to 333.15 K. The model contains only two parameters; they are shown to be independent of an arbitrarily chosen reference state. The parameters show a slight dependence on temperature, but this dependence is ignored in computations to demonstrate the rigor of the IILM in predicting CO<sub>2</sub> solubility at high and low pressures at various temperatures. Model predictions are compared against the experimental data of Anthony et al. (*J. Phys. Chem. B* **2002**, 106, 7315) and of Blanchard et al. (*J. Phys. Chem. B* **2001**, 105, 2437). The usefulness of the model is in predicting CO<sub>2</sub> solubilities at temperatures and pressures where experimental data are unavailable.

## Introduction

Room-temperature ionic liquids exhibit unusual solvent properties such as extremely low vapor pressure, thermal stability, and immiscibility with a number of organic solvents.<sup>1–5</sup> They consist of organic cations bonded in seemingly endless combinations with anions such as PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, Cl<sup>−</sup>, etc. The industrial potential of ionic liquids in catalysis, chemical synthesis, and separation technology<sup>6–8</sup> and as electrolytes in batteries and sensors<sup>9</sup> is being actively researched. Experimental data on gas solubilities in ionic liquids, useful for potential applications to gas separations, are becoming available in the literature; thermodynamic means for the prediction of gas solubilities are lacking. In this paper, an approach using the irregular ionic lattice model (IILM) to predict the vapor pressure and solubility of gases in ionic liquids is set forth. The model is applied to the solubility of carbon dioxide in two ionic liquids that have been studied extensively by Blanchard et al.<sup>10</sup>

The irregular ionic lattice model is essentially a two-parameter model in which CO<sub>2</sub> is considered the “solute”

and the ionic liquid is the “solvent”. The main feature of the model is the construction of an expression yielding the total number of microstates ( $\Omega$ ) associated with all configurations possible when  $N$  distinguishable solute and solvent particles share a fixed amount of energy. The derivation of  $\Omega$  is not trivial and has been discussed elsewhere.<sup>11–14</sup>

Maximizing the entropy of the system (solute + solvent) under the energy constraint using the Lagrangian multiplier method ultimately yields a free energy function that is extensive and homogeneous in the number of solute (gas, such as CO<sub>2</sub>) and solvent (ionic liquid) particles that comprise the system. The derived chemical potentials must, and in fact do, satisfy the Gibbs–Duhem relation, as has been demonstrated for binary and ternary aqueous electrolytes.

In the application to the CO<sub>2</sub>–ionic liquid system, carbon dioxide molecules are considered “bound” to the ionic liquid in monolayer adsorption or in contact with other carbon dioxide molecules in “free” multilayer adsorption. The excess internal energy of a bound CO<sub>2</sub> molecule relative to the internal energy of a free molecule is denoted by  $\epsilon$  and is one of two parameters used in the model. The second parameter, denoted by  $r$ , describes the average number of dissolved carbon dioxide molecules associated with each molecule of the ionic liquid. The standard states are (1) pure ionic liquid and (2) pure liquid carbon dioxide. The latter is clearly a hypothetical standard state unrealizable in practice, especially if the temperature of the mixture exceeds the critical temperature (304.2 K) of carbon dioxide.

To exemplify the predictive nature of the theory, in this paper, the two parameters,  $r$  and  $\epsilon$ , are obtained from sparse data<sup>10</sup> and are kept constant with respect

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to temperature and concentration of dissolved carbon dioxide. Carbon dioxide solubility is then predicted in the temperature ranges of 298.15–323.15 K for the ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) and 313.15–323.15 K for 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C8mim][BF<sub>4</sub>]) and compared against available experimental data at elevated pressure from Blanchard et al.<sup>10</sup> and at low pressure from Anthony et al.<sup>15</sup> Even though both parameters should exhibit a slight dependence on temperature,<sup>16–18</sup> they are kept constant in this study to emphasize the usefulness of the model to provide solubility and vapor pressure information when such information is laborious, expensive, and time-consuming to obtain experimentally.

### Thermodynamics of CO<sub>2</sub>–Ionic Liquids: Model Parameters Independent of Reference States

The thermodynamic activity of CO<sub>2</sub> dissolved in an ionic liquid (IL) is postulated to be given by the same relationship<sup>11,12,16–18</sup> as that derived for aqueous electrolytes, except for certain peculiarities in the standard states encountered for the CO<sub>2</sub>–IL system that are absent in the case of aqueous electrolytes. The relationship between the dissolved CO<sub>2</sub> activity,  $a^{\text{IL}}$ , and the CO<sub>2</sub> mole fraction in solution,  $x$ , is given by

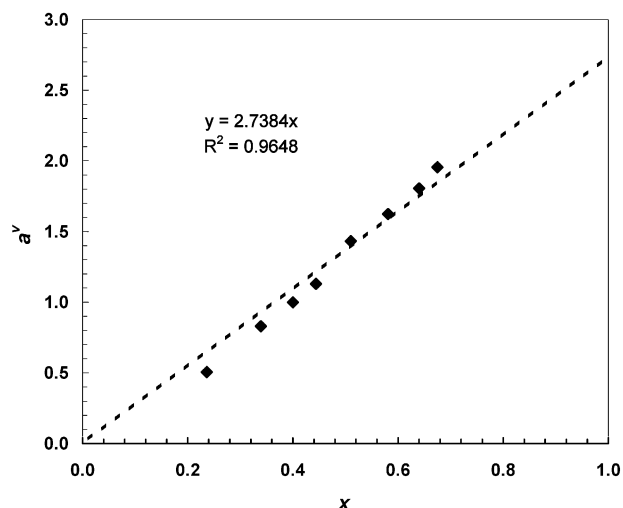
$$\frac{a^{\text{IL}}(1-x)}{x(1-a^{\text{IL}})} = \frac{1}{cr} + \frac{(c-1)a^{\text{IL}}}{cr} \quad (1)$$

where  $a^{\text{IL}}$  is the thermodynamic activity of dissolved CO<sub>2</sub> in the IL;  $c = \exp(-\epsilon/RT)$ ;  $R$  is the universal gas constant ( $8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ );  $T$  is the absolute temperature of the solution; and  $r$  and  $\epsilon$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) are parameters, as discussed above. The standard state for dissolved CO<sub>2</sub> is most conveniently chosen to be the pure liquid at the temperature and pressure of the solution, but in the case of CO<sub>2</sub>–IL systems, pure liquid CO<sub>2</sub> does not exist above 304.2 K, and therefore, the CO<sub>2</sub> fugacity cannot be readily established. This problem is overcome by making an arbitrary choice of the reference state taken at a fixed composition and then calculating the activity of dissolved CO<sub>2</sub> with respect to this reference state. In this manner, it is possible to utilize eq 1 along with sparse experimental data to extract the two parameters,  $r$  and  $\epsilon$ , in a meaningful and consistent way. The arbitrarily chosen reference state is taken as  $x = 0.400$ . To ensure that this unconventional method of calculating the dissolved CO<sub>2</sub> activity is valid, we recalculate the parameters using another arbitrarily selected reference state of  $x = 0.236$  and show that the parameters  $r$  and  $\epsilon$  remain unchanged; that is, these parameters are essentially independent of the choice of reference states, as they must be.

The chemical equilibrium between CO<sub>2</sub> in the vapor phase and that dissolved in the IL is given by  $\mu^{\text{v}} = \mu^{\text{IL}}$ , where  $\mu$  represents the chemical potential of CO<sub>2</sub> and the superscripts v and IL represent the vapor and condensed (liquid mixture) phases, respectively. Expansion of the chemical equilibrium condition gives

$$\mu^0(y=1, T, P) + RT \ln a^{\text{v}}(y, T, P) = \mu^*(x=1, T, P) + RT \ln a^{\text{IL}}(x, T, P) \quad (2)$$

Slight rearrangement of eq 2 gives the desired relationship between the thermodynamic activities of CO<sub>2</sub> in



**Figure 1.** Experimental data of Blanchard et al., extrapolated to  $x = 1$ , for [bmim][PF<sub>6</sub>]-CO<sub>2</sub> at 323.15 K yields an activity of CO<sub>2</sub> in the vapor phase (hypothetical) of  $a^{\text{v}} \approx 2.74 \pm 0.06$ . The reference state is  $x = 0.400$ ,  $T = 323.15 \text{ K}$ , at which the CO<sub>2</sub> fugacity is 32.64 bar.

the vapor and dissolved phases

$$RT \ln \left[ \frac{a^{\text{v}}}{a^{\text{IL}}} \right] = (\mu^* - \mu) \quad (3)$$

Because the right-hand side (rhs) of eq 3 is independent of composition, the value of the ratio  $a^{\text{IL}}/a^{\text{v}}$  at any composition suffices to quantify the rhs of eq 3. We arbitrarily choose the activity (hypothetical) of pure liquid CO<sub>2</sub>,  $a^{\text{IL}}(x=1, T, P) = 1$ . Extrapolating experimental vapor pressure data of Blanchard et al. at 323.15 K converted to activities,  $a^{\text{v}}$ , with respect to the arbitrarily chosen reference state of  $x = 0.400$  where the CO<sub>2</sub> fugacity is 32.64 bar, the value for the activity of pure CO<sub>2</sub> in the vapor phase,  $a^{\text{v}}(y=1, T, P)$  can be extracted by extrapolating linearly to  $x = 1$ , as shown in Figure 1. An estimate of the slope at the 95% confidence interval using the two-sided *t*-test is  $2.74 \pm 0.06$ . Substituting the value of  $a^{\text{v}} = 2.74 \pm 0.06$  into eq 3 yields  $(\mu^* - \mu) = \Delta\mu = 2.72 \pm 0.059 \text{ kJ}\cdot\text{mol}^{-1}$  at 323.15 K.

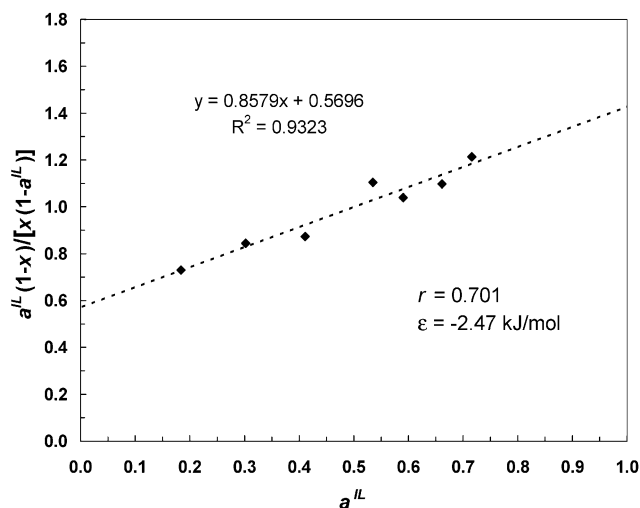
Because  $\Delta\mu$  is independent of the solution composition at constant temperature, the ratio of the activity of CO<sub>2</sub> in the vapor phase,  $a^{\text{v}}$ , to the activity of CO<sub>2</sub> in the IL,  $a^{\text{IL}}$ , will also remain constant, according to eq 3. Thus, it is possible to extract  $a^{\text{IL}}$  using eq 3 and  $a^{\text{v}}$  from experimental data, from which the parameters  $r$  and  $\epsilon$  can be obtained using eq 1. The calculated values of  $a^{\text{IL}}$  as a function of dissolved CO<sub>2</sub> mole fraction,  $x$ , are presented in Table 1. Linear regression by the method of least squares of  $a^{\text{IL}}(x^{\text{IL}})/[x(1-a^{\text{IL}})]$  plotted on the ordinate and  $a^{\text{IL}}$  on the abscissa, as in Figure 2, yields a slope equal to  $(c-1)/cr$  and an intercept equal to  $1/cr$ , from which  $r$  and  $c$  can be readily obtained. Note that  $a^{\text{IL}}$  is dependent on  $a^{\text{v}}$  by eq 3 and  $a^{\text{v}}$ , in turn, is dependent on the reference state. The ratio  $a^{\text{v}}/a^{\text{IL}} \approx 2.75$  remains essentially the same for all compositions of the CO<sub>2</sub>–[bmim][PF<sub>6</sub>] mixture to satisfy eq 3. The parameter  $\epsilon$  is obtained from  $c = \exp(-\epsilon/RT)$ . For [bmim][PF<sub>6</sub>], the data of Blanchard et al.<sup>10</sup> yield  $r = 0.701 \pm 0.265$  and  $\epsilon = -2.466 \pm 0.46 \text{ kJ}\cdot\text{mol}^{-1}$  at 323.15 K.

To demonstrate that both  $r$  and  $\epsilon$  remain independent of the unconventional choice of reference state for the same system, CO<sub>2</sub>–[bmim][PF<sub>6</sub>], we choose another

**Table 1. Activity of CO<sub>2</sub> in [bmim][PF<sub>6</sub>] at 323.15 K Referenced to  $x = 0.400$ , Used to Obtain Parameters from the Irregular Ionic Lattice Model Using Eq 1<sup>a</sup>**

$x^b$	$a^v^c$	$a^{IL}^d$	$a^{IL}(x_{IL})/[x(1 - a^{IL})]$
0.236	0.506	0.184	0.730
0.339	0.831	0.302	0.844
0.444	1.130	0.411	0.874
0.51	1.471	0.535	1.105
0.581	1.624	0.590	1.039
0.64	1.819	0.661	1.098
0.675	1.969	0.716	1.213

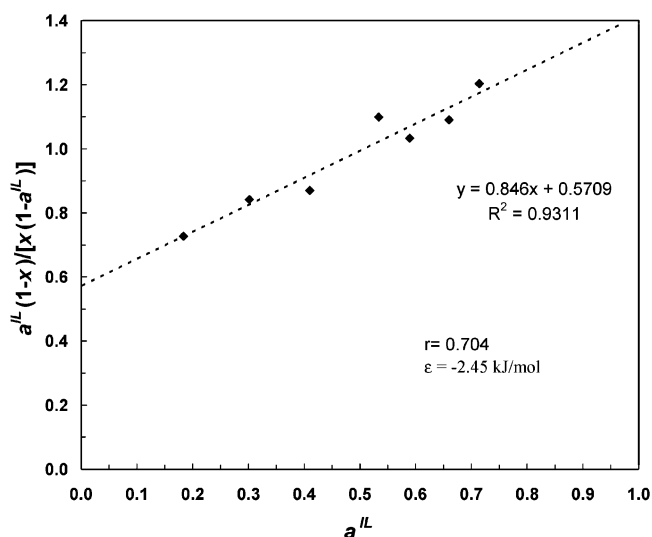
<sup>a</sup> Reference-state CO<sub>2</sub> fugacity = 32.21 bar. <sup>b</sup> Compositions from Blanchard et al.<sup>10</sup> <sup>c</sup> Calculated with respect to an arbitrarily selected reference state. <sup>d</sup> Calculated using eq 3.

**Figure 2.** IILM plot for the system CO<sub>2</sub>–[bmim][PF<sub>6</sub>] at 323.15 K, yielding the model parameters  $r$  and  $\epsilon$ . The reference state is  $x = 0.400$ , at which the CO<sub>2</sub> fugacity is 32.64 bar (Sandler<sup>19</sup>).**Table 2. Activity of CO<sub>2</sub> in [bmim][PF<sub>6</sub>] at 313.15 K Referenced to  $x = 0.236$ , Used to Obtain Parameters from the Irregular Ionic Lattice Model Using Eq 1<sup>a</sup>**

$x^b$	$a^v^c$	$a^{IL}^d$	$a^{IL}(x_{IL})/[x(1 - a^{IL})]$
0.236	1.00	0.184	0.728
0.339	1.643	0.301	0.841
0.444	2.235	0.410	0.870
0.51	2.909	0.534	1.099
0.581	3.211	0.589	1.033
0.64	3.395	0.660	1.090
0.675	3.893	0.714	1.203

<sup>a</sup> Reference-state CO<sub>2</sub> fugacity = 16.51 bar (Sandler<sup>19</sup>). <sup>b</sup> From experimental data of Blanchard et al.<sup>10</sup> <sup>c</sup> Calculated with respect to an arbitrarily selected reference state.<sup>3</sup> <sup>d</sup> Calculated from eq 3.

reference state at  $x = 0.236$ ,  $T = 323.15$  K, where the CO<sub>2</sub> fugacity is 16.51 bar, and generate Table 2 and Figure 3 as in the previous case of the reference state,  $x = 0.400$  and  $T = 323.15$  K. The ratio  $a^v/a^{IL} \approx 5.45$  remains essentially constant for all compositions of the CO<sub>2</sub>–[bmim][PF<sub>6</sub>] mixture in Table 2. The IILM model parameters when the reference state is shifted to  $x = 0.236$  are  $r = 0.704 \pm 0.265$  and  $\epsilon = -2.45 \pm 0.457$  kJ·mol<sup>-1</sup>, which are essentially the same as for the case when the reference state is at  $x = 0.400$ , thus validating the approach. In comparison to aqueous electrolytes containing dissolved inorganic salts, the  $r$  values for CO<sub>2</sub> in ILs are somewhat lower. For single salts such as LiBr, Ca(NO<sub>3</sub>)<sub>2</sub>, and LiNO<sub>3</sub>, the  $r$  values are in the neighborhood of 3 at 298.15 K and decrease slightly at higher temperatures. However, the situation for reciprocal salts is quite different. For (Li,K)NO<sub>3</sub>, (Ca,K)NO<sub>3</sub>,

**Figure 3.** IILM plot for the system CO<sub>2</sub>–[bmim][PF<sub>6</sub>] at 323.15 K, yielding the model parameters  $r$  and  $\epsilon$ . The reference state is  $x = 0.236$ , at which the CO<sub>2</sub> fugacity is 16.51 bar (Sandler<sup>19</sup>).**Table 3. Parameters  $r$ ,  $\epsilon$ , and  $\Delta\mu$  as Functions of Temperature for the CO<sub>2</sub>–[Bmim][PF<sub>6</sub>] System, Evaluated with Respect to the Reference State Composition of  $x = 0.400$** 

parameter	temperature (K)		
	313.15	323.15	333.15
$r$	0.687	0.704	0.621
$\epsilon$ (kJ·mol <sup>-1</sup> )	-2.49	-2.47	-3.47
$\Delta\mu$ (kJ·mol <sup>-1</sup> )	2.38	2.67	2.80

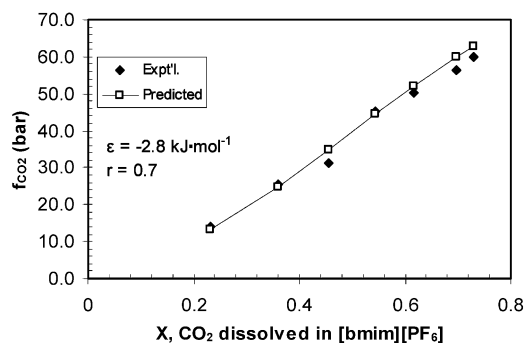
and (Li,K,Na)NO<sub>3</sub>, Braunstein and Braunstein<sup>17</sup> report experimentally measured  $r$  values of 1.7, 2.0, and 2.0, respectively, at 393.15 K. The  $r$  parameter for KNO<sub>3</sub> at 393.15 K is computed<sup>18</sup> to be 0.7. Therefore,  $r$  values <0.7 for an IL are not extraordinarily small, but they do signify a smaller number of CO<sub>2</sub> molecules associated with the IL as compared to electrolytes in water. Small  $r$  values for CO<sub>2</sub>–IL systems are plausible on the basis of smaller electrostatic interactions between CO<sub>2</sub> and ILs as compared to those between completely dissociated electrolytes and water.

Evaluations of the IILM parameters at other temperatures are summarized in Table 3 and indicate a small dependence on temperature.<sup>16,17</sup> To demonstrate the model's rigor, validity, and usefulness, we accept average values of  $r = 0.7$  and  $\epsilon = -2.8$  kJ·mol<sup>-1</sup> and use them to compare model predictions to experimental data and to generate data at temperatures, compositions, and pressures beyond those utilized to evaluate the two parameters. CO<sub>2</sub> solubilities from low (less than 1 bar) to high (up to 65 bar) pressures are predicted successfully.

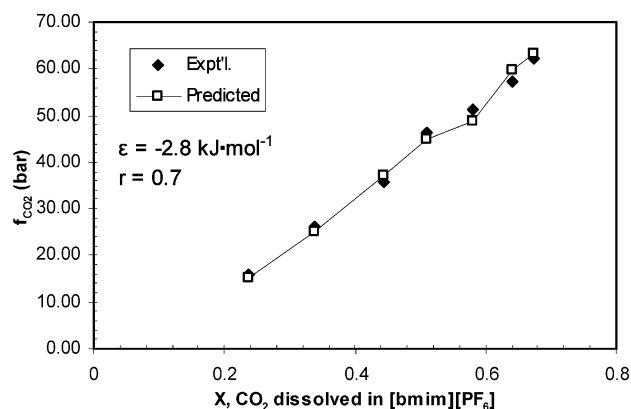
### Predicted and Experimental Solubilities for the System CO<sub>2</sub>–[bmim][PF<sub>6</sub>]

To predict the CO<sub>2</sub> solubility in [bmim][PF<sub>6</sub>] at conditions other than those for which the model parameters were estimated, eq 1 is solved for  $a^{IL}$  with the stated values of the parameters,  $r = 0.7$  and  $\epsilon = -2.8$  kJ·mol<sup>-1</sup>. The CO<sub>2</sub> vapor-phase activity,  $a^v$ , is subsequently obtained from eq 3, as  $a^{IL}$  and  $\Delta\mu$  are known. Note that  $\Delta\mu$  is dependent on the choice of reference states, arbitrarily chosen as  $x = 0.400$  for these calculations. The fugacity of CO<sub>2</sub> is then,  $f^v = (a^v)^{f^0}$ . Figures 4





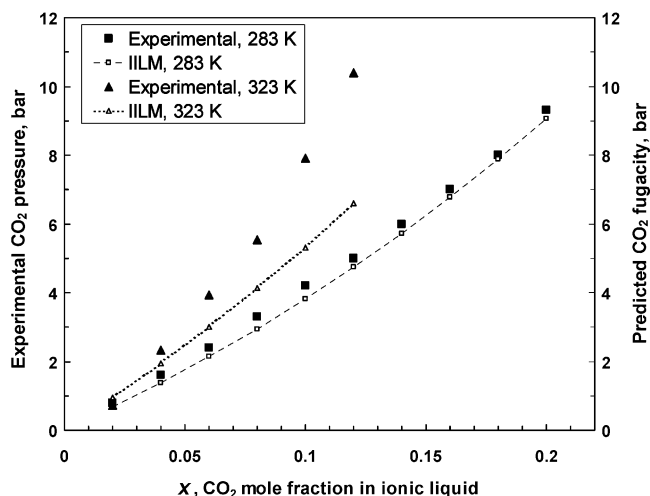
**Figure 4.** Comparison of predicted and experimental solubilities of CO<sub>2</sub> in [bmim][PF<sub>6</sub>] at 313.15 K. Data are from ref 10; prediction is based on the average values  $\epsilon = -2.8 \text{ kJ}\cdot\text{mol}^{-1}$  and  $r = 0.7$ , derived from data at 323.15 K.



**Figure 5.** Comparison of predicted and experimental solubilities of CO<sub>2</sub> in [bmim][PF<sub>6</sub>] at 323.15 K. Data are from ref 10; prediction is based on the average values  $\epsilon = -2.8 \text{ kJ}\cdot\text{mol}^{-1}$  and  $r = 0.7$ , derived from data at 323.15 K.

and 5 show agreement between the predicted and experimental data. Generalized fugacity coefficients<sup>18</sup> of pure gases and liquids were used to obtain the fugacities.

The ability to predict CO<sub>2</sub> solubilities in ILs is further demonstrated by computing solubilities at significantly lower pressures than the conditions at which the model parameters were estimated for this system. Recently, Anthony et al.<sup>15</sup> reported experimental data on the solubility of CO<sub>2</sub> in [bmim][PF<sub>6</sub>] at 283.15 K, where the CO<sub>2</sub> pressure is relatively low. This set of data seemed to represent a reasonable test of the IILM if low-pressure, low-temperature solubilities could be predicted from the same parameters ( $r = 0.7$ ,  $\epsilon = -2.8 \text{ kJ}\cdot\text{mol}^{-1}$ ) as used for higher temperatures and pressures, as discussed above. The results of the solubility calculations are plotted in Figure 6 with values of the experimental CO<sub>2</sub> pressures in bars, read (accurate to no more than  $\pm 0.2$  bar) from an enlarged image of the graph in Anthony et al.<sup>15</sup> Because the fugacity coefficients of CO<sub>2</sub> at 283.15 K and low pressures ( $< 8$  bar) are on the order of unity, no attempt is made to convert calculated fugacities to bars in light of the fact that the conversion would be materially obscured by the error ( $\pm 0.2$  bar) in reading the magnitude of the experimental data. Therefore, this minor correction is ignored because it is not important in emphasizing the value of the IILM in predicting CO<sub>2</sub> solubilities at temperature and pressures not used in evaluating the two model parameters. Excellent agreement between experiment and the IILM model regarding solubilities was obtained at 283.15 K,



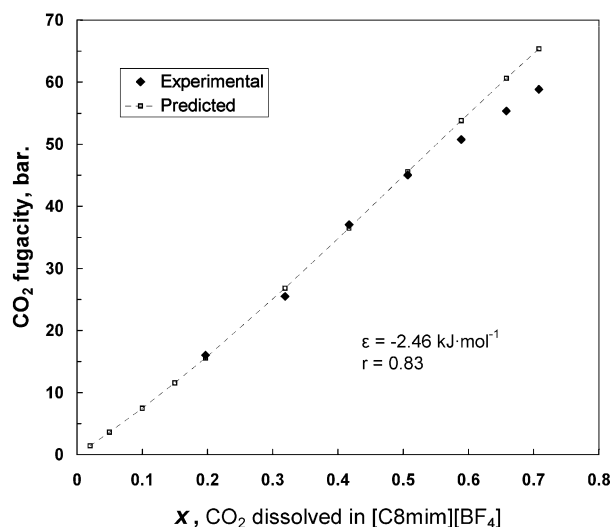
**Figure 6.** Comparison of predicted and experimental CO<sub>2</sub> solubilities and Henry's constants in [bmim][PF<sub>6</sub>] at low CO<sub>2</sub> pressures. The experimental Henry's constant for 283.15 K is reported<sup>15</sup> as  $38.7 \pm 0.4$  bar, whereas the IILM model yields a Henry's constant of 35 bar. At 323.15 K, experimental Henry's constant is  $81.3 \pm 0.5$  bar versus 75 bar predicted by the model. Data are from refs 10 and 15. Parameters used for the IILM predictions are  $r = 0.7$  and  $\epsilon = -2.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

notwithstanding the fact that the model is seen to overpredict the carbon dioxide solubility in [bmim][PF<sub>6</sub>] at 323.15 K. If the model parameters are modified to include the small dependence on temperature, the predictions could be further improved. However, these incremental improvements are not the goal of the paper.

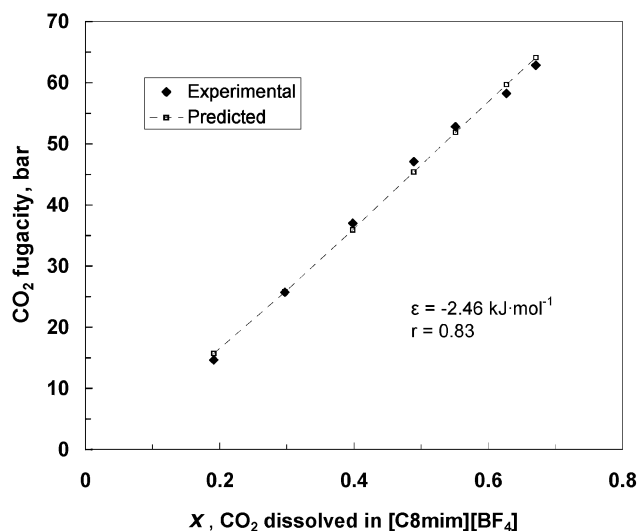
The agreement between experimentally determined Henry's constants [ $H = \lim_{x \rightarrow 0} (f^L/x)$ ] and model predictions for CO<sub>2</sub> in [bmim][PF<sub>6</sub>] is quite good. Henry's constant from the IILM is obtained from the limiting value of the slope of a plot of the CO<sub>2</sub> fugacity versus the dissolved CO<sub>2</sub> mole fraction. The experimental Henry's constant at 283.15 K is reported<sup>15</sup> as  $38.7 \pm 0.4$  bar, whereas the IILM model yields a Henry's constant of 35 bar; in addition, the experimental Henry's constant at 323.15 K of  $81.3 \pm 0.5$  bar is in reasonable agreement with the model prediction of 75 bar at 323.15 K.

### Predicted and Experimental Solubilities for the System CO<sub>2</sub>–[C8mim][BF<sub>4</sub>]

The solubility of CO<sub>2</sub> in [C8mim][BF<sub>4</sub>] is obtained in a manner identical to that used for CO<sub>2</sub>–[bmim][PF<sub>6</sub>] mixtures. The two parameters are estimated to be  $r = 0.83$  and  $\epsilon = -2.46 \text{ kJ}\cdot\text{mol}^{-1}$ . Comparisons between the experimental and predicted solubilities of CO<sub>2</sub> in [C8mim][BF<sub>4</sub>] at 313.15 and 323.15 K are shown in Figures 7 and 8, respectively. The agreement between the experimental and predicted results is very good, despite some deviations at the high end of the dissolved CO<sub>2</sub> mole fraction, in excess of 0.6. The true cause of these deviations is undetermined and requires further investigation. Figures 2 and 3 provide a clue to the answer by indicating the presence of random experimental errors. It is possible that there is also a relative systematic error in the experimental procedure that becomes more pronounced at high CO<sub>2</sub> mole fractions. On the other hand, the nature of the bonding between CO<sub>2</sub> and ILs might be qualitatively different from what the IILM assumes.



**Figure 7.** Comparison of predicted and experimental solubilities in  $\text{CO}_2$ -[C8mim][BF<sub>4</sub>] mixtures at 313.15 K. Experimental data are from ref 10.



**Figure 8.** Comparison of predicted and experimental solubilities in  $\text{CO}_2$ -[C8mim][BF<sub>4</sub>] mixtures at 323.15 K. Experimental data are from ref 10.

## Conclusions

The irregular ionic lattice model is successfully applied to predict the solubilities of  $\text{CO}_2$  in [bmim][PF<sub>6</sub>] and in [C8mim][BF<sub>4</sub>] across wide pressure and temperature ranges. For simplicity and to demonstrate the rigor of the model, the parameters ( $r$  and  $\epsilon$ ) are maintained independent of temperature, pressure, and composition. Predicting the  $\text{CO}_2$  solubility in [bmim][PF<sub>6</sub>] at 298.15 K (high pressure) and the  $\text{CO}_2$  solubility in [bmim][PF<sub>6</sub>] at 283.15 K (low pressures) without altering the parameters demonstrates the model's flexibility. Agreement between experimental and predicted Henry's constant is also good. The  $\text{CO}_2$ -IL system presents peculiarities in defining a reference state for thermodynamic calculations. We demonstrate that the model parameters are independent of the choice of reference states. Because liquid  $\text{CO}_2$  is hypothetical at room temperature and pressure, its thermodynamic activity is not easily defined. This obstacle is overcome by adopting an arbitrarily chosen composition as the reference state at which the  $\text{CO}_2$  vapor pressure is known to define the reference state fugacity. In prin-

ciple, only two experimental data are needed to obtain the parameters and apply the IILM to a single IL- $\text{CO}_2$  system. In practice, experimental data and measurements are subject to systematic and random errors, and hence, several data points are needed to obtain the necessary parameters with acceptable confidence. Modeling and experiments on other ionic liquids, including ternary mixtures, are underway.

Although the IILM has been shown to be successful in predicting  $\text{CO}_2$  solubilities over large composition, temperature, and pressure ranges, this model has its limitations. The first limitation to bear in mind is that the model holds as long as the assumed irregular ionic lattice structure of the  $\text{CO}_2$ -IL system is valid. In the limiting case approaching pure  $\text{CO}_2$ , the irregular ionic structure must break down (practically ceases to exist), as does the model. Therefore, the results of this paper should not be extrapolated to the limiting case of pure  $\text{CO}_2$ . The underprediction of the  $\text{CO}_2$  pressure at 323 K in Figure 6 might be a result of ignoring the temperature dependence of the model parameters, or errors in the experimental data, or both. Additional data on ionic liquids from different research laboratories might shed light on this issue.

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## Nomenclature

- $a^{\text{IL}}$  = thermodynamic activity of  $\text{CO}_2$  in the IL
- $a^{\text{v}}$  = thermodynamic activity of  $\text{CO}_2$  in the vapor phase
- $c$  = modified IILM parameter defined in the text
- $f^{\text{v}}$  = fugacity of  $\text{CO}_2$  vapor, bar
- $f^{\text{v}^0}$  = fugacity of  $\text{CO}_2$  at the reference state, bar
- $f^{\text{L}}$  = fugacity of liquid in equilibrium with vapor, bar
- IL = ionic liquid, [bmim][PF<sub>6</sub>] or [C8mim][BF<sub>4</sub>]
- $P$  = total pressure, bar
- $r$  = IILM parameter
- $R$  = universal gas constant,  $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- $T$  = absolute temperature, K
- $x$  = mole fraction of  $\text{CO}_2$  in the IL
- $x^{\text{IL}}$  = mole fraction of the IL,  $x^{\text{IL}} = (1 - x)$
- $y$  = mole fraction of  $\text{CO}_2$  in the vapor phase

### Greek Letters

- $\epsilon$  = IILM parameter,  $\text{kJ}\cdot\text{mol}^{-1}$
- $\mu^*$  = chemical potential of pure liquid (hypothetical)  $\text{CO}_2$  at the temperature and pressure of the solution
- $\mu^{\text{v}}$  = chemical potential of pure  $\text{CO}_2$  vapor at the temperature and pressure of the solution
- $\Delta\mu$  = difference in reference-state Gibbs free energy,  $(\mu^* - \mu)$ ,  $\text{kJ}\cdot\text{mol}^{-1}$

## Literature Cited

- (1) Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351-358.

- (2) Ionic Liquids Prove Increasingly Versatile. *Chem. Eng. News*, 1999, 77, 23–24.
- (3) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, 99, 2071–2084.
- (4) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. *Chem. Rev.* **2002**, 102, 3667–3692.
- (5) Wasserscheid, P.; Keim, W. Ionic Liquids—New “Solutions” for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, 39, 3773–3789.
- (6) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. Traditional Extractants in Nontraditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2000**, 39, 3596.
- (7) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green processing using ionic liquids and CO<sub>2</sub>. *Nature* **1999**, 399, 28–29.
- (8) Dai, S.; Ju, Y. H.; Barnes, C. E. Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J. Chem. Soc., Dalton Trans.* **1999**, 1201–1202.
- (9) Liang, C. D.; Yuan, C. Y.; Warmack, R. J.; Barnes, C. E.; Dai, S. Ionic liquids: A new class of sensing materials for detection of organic vapors based on the use of a quartz crystal microbalance. *Anal. Chem.* **2002**, 74, 2172–2176.
- (10) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Behavior of Ionic Liquid/CO<sub>2</sub> Systems. *J. Phys. Chem. B* **2001**, 105, 2437–2444.
- (11) Ally, M. R.; Braunstein, J. Statistical mechanics of multilayer adsorption: Electrolyte and water activities in concentrated solutions. *J. Chem. Thermodyn.* **1998**, 30, 49–58.
- (12) Braunstein, J.; Ally, M. R. On the Abraham Equation for Salt Activities in Concentrated Solutions. *Monatsh. Chem.* **1996**, 127, 269–273.
- (13) Abraham, M. L'activité d'un sel à hautes concentrations dans l'eau pure. *J. Chim. Phys.* **1981**, 78 (1), 57–59.
- (14) Mayer, J. E.; Mayer, M. G. *Statistical Mechanics*; Wiley: New York, 1940.
- (15) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, 106, 7315.
- (16) Stokes, R. H.; Robinson, R. A. Ionic Hydration and Activity in Electrolyte Solutions. *J. Am. Chem. Soc.* **1948**, 70, 1870–1878.
- (17) Braunstein, H.; Braunstein, J. Isopiestic studies of very concentrated aqueous electrolyte solutions of LiCl, LiBr, LiNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>3</sub> + KNO<sub>3</sub>, LiNO<sub>3</sub> + CsNO<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> + CsNO<sub>3</sub> at 100 to 150 °C. *J. Chem. Thermodyn.* **1971**, 3, 419–431.
- (18) Ally, M. R.; Braunstein, J. BET model for calculating activities of salts and water, molar enthalpies, molar volumes and liquid–solid phase behavior in concentrated electrolyte solutions. *Fluid Phase Equilib.* **1993**, 87, 213–236.
- (19) Sandler, S. I. *Chemical and Engineering Thermodynamics*; Wiley: New York, 1977.

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