Solubility of Carbon Dioxide in 1-Ethyl-3-methylimidazolium Tetrafluoroborate

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The solubility of carbon dioxide in the room-temperature ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium tetrafluoroborate for temperatures ranging from (303.2 to 343.2) K and pressures below 5 MPa were measured using a thermogravimetric microbalance. The gas solubilities were determined from absorption saturation (equilibrium) data at each temperature and pressure. The buoyancy effect was accounted for in the evaluation of the gas solubilities. An accurate equation of state and density equation for carbon dioxide and ionic liquids, respectively, were employed to determine the effect of buoyancy on the gas solubilities. The carbon dioxide solubilities in ionic liquids are presented as a function of temperature and pressure. The experimental solubility pressure data of carbon dioxide in the ionic liquids was successfully represented using an extended Henry's law correlation.

Introduction

In recent years, global warming had been a serious environmental problem, and the increasing accumulation of CO_2 in the atmosphere is believed to be one of the major contributors. Thus, developing efficient methods for capturing CO_2 from gas streams in chemical processes is critically important. The use of aqueous solutions of alkanolamines (organic solvents with $-NH_2$) is one of the most widely applied technologies for removing CO_2 industrially via chemical absorption.[1] Although these aqueous alkanolamine solutions are industrially effective on CO_2 removal, this method has several serious drawbacks such as intensive energy consumption, cost increases, and corrosion problems. In this regard, it is necessary to find a new kind of sequestering agent, and to this end, a new class of solvents, referred to as room-temperature ionic liquids (RTILs), may offer at least a partial solution to these problems.

RTILs are a combination of bulky, asymmetric N-containing organic cations (such as imidazole, pyrrole, pyridine, and quarternary ammonium) and anions of wide variety, which range from simple inorganic ions (such as halides) to more complex organic species (such as bis[(trifluoromethyl)sulfonyl]imide). Due to their unique properties, such as low volatility, nonflammability, high thermal stability, and high solvation capacity,[2−4] RTILs have been recognized as a versatile alternative to conventional organic solvents. RTILs are also termed green and designer solvents because the mentioned properties have lesser degrading effects on the environment and can be custom-fitted for specific applications.

Solubility studies are essential to chemical separation processes because knowledge of solvent-phase behaviors will help determine the attractiveness of using these solvents for specific applications, such as in the case for CO_2 in RTILs.[5] Thus, in recent years, the amount of experimental and theoretical work on such properties has increased considerably. Many studies have focused on imidazolium RTILs, but only over a limited temperature and pressure range.[5−26]

Different experimental methods such as the closed cell (static) method, chromatography, phase equilibration, pressure change measurement, volumetric, and gravimetric[5,23−26] can be applied to measure the gas solubility in a solvent. The closed cell method and phase equilibration require a longer period of time. Chromatography, pressure change measurement, and volumetric techniques are faster methods but less accurate. On the other hand, the measurement of gas solubility using the gravimetric method seems to be the simplest technique to use and is reasonably accurate.

In this work, the equilibrium solubility data of CO_2 in RTILs 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF_6] and 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF_4] for a temperature range of (303.2 to 343.2) K and pressures below 5 MPa were measured using a thermogravimetric microbalance. The effect of buoyancy was accounted for in the evaluation of CO_2 solubilities. Buoyancy correction requires knowledge of high-pressure density data of the gas and the solvent. In this regard, the accurate equation of state and the density equation for CO_2 and RTIL, respectively, were employed. For systems in which literature values of CO_2 solubilities in RTILs were available, a comparison was made to show that the measured data in this work agree. The experimental solubility pressures were modeled using an extended Henry's law correlation.

Experimental Section

Chemicals. The RTIL samples were supplied by TCI Co. with a minimum purity of 99.0 % and 97.0 % for [Bmim][PF_6] and [Emim][BF_4], respectively. The water mass fraction of the samples as stated by the supplier were 0.002 and 0.009 for [Bmim][PF_6] and [Emim][BF_4], respectively. The RTILs were degassed inside the vessel of the microbalance where it was heated (343.2 K) in a vacuum for 8 h to remove any volatile impurities. Research grade CO_2 was supplied by Liehwa Industrial Gases, (KUN Technology, Co., Ltd.), with a minimum purity of 99.9 %.

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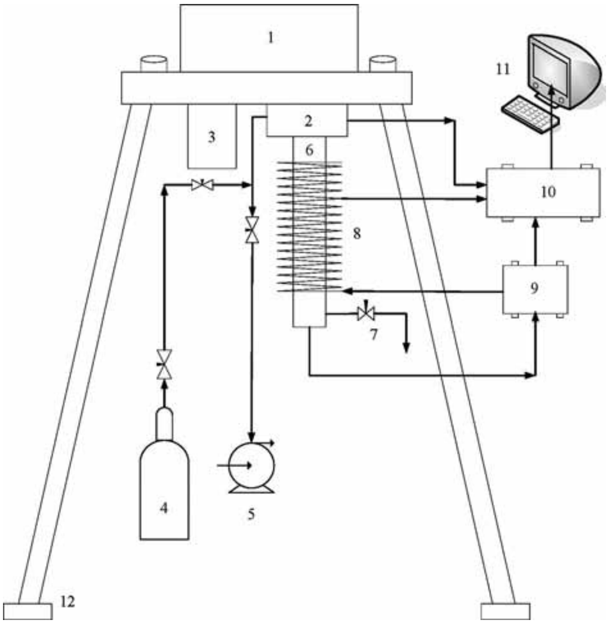

Figure 1. Experimental setup for CO_2 solubility using a thermogravimetric microbalance: 1, electrobalance; 2, sample side; 3, tare side; 4, CO_2 source; 5, vacuum pump; 6, reactor vessel; 7, gas output; 8, thermostatic coil; 9, automatic temperature controller; 10, digital recording balance; 11, computer output; and 12, microbalance support base.

Carbon Dioxide Solubility Measurements. The CO_2 solubility was measured using a thermogravimetric microbalance (model D-110, Thermo Cahn Co.), with experimental setup shown in Figure 1. To have a fully automatic and reproducible result of gas absorption−desorption isotherms the Thermo Cahn design integrates precise computer control and measurement of mass change, pressure, and temperature. The microbalance consists of a highly sensitive electrobalance with sample and counterweight components inside a stainless steel pressure vessel. The balance has a mass range of up to 100 g with a readability of 1 μg. The maximum temperature and pressure the balance can hold were 848.2 K and 10.34 MPa, respectively. The microbalance has the following uncertainty: mass is $\pm 1 \cdot 10^{-6}$ g, temperature ± 0.1 K, and pressure $\pm 7 \cdot 10^{-5}$ MPa. The uncertainty of the solubility measurements using the microbalance was $\pm 1 \cdot 10^{-4}$ (on a molality scale). It can operate in both dynamic and static modes. Dynamic mode operation allows a continuous flow of gas past the sample, while the static mode operation introduces gas into the top of the balance and the reactor vessel is closed. In this work, all absorption measurements were performed in the static mode.

Approximately 200 μL of the sample (RTIL) was loaded on the microbalance pan using a micropipette, and the vessel was sealed. The sample was dried and degassed by first pulling a coarse vacuum on the sample with a diaphragm pump and then fully evacuating the reactor to a minimum of 10^{-6} Pa with a turbopump (model CDK 180 Turbomolecular pump, ILMVAC Co.). While under vacuum, the sample was heated to 343.2 K for a minimum of 8 h with an external heating coil surrounding the vessel connected to a remote-controlled temperature controller (model Digital Controller CB900, RKC Instrument Inc.). Then the CO_2 was introduced slowly into the top of the vessel to the desired pressure, and then the input gas valve was closed. After the introduction of the gas, the desired temperature (from high T to low T) was then set, and the system was allowed to reach equilibrium. To ensure sufficient time for gas−liquid equilibrium, normally the IL sample was maintained at constant temperature for a minimum of 8 h (until the mass is approximately constant). Upon completion of the set of temperatures, the pressure was raised to the next target pressure, and the procedure was repeated accordingly. The digital recording balance (DRB) of the Thermo Cahn automatically records the data after setting the next desired temperature and pressure.

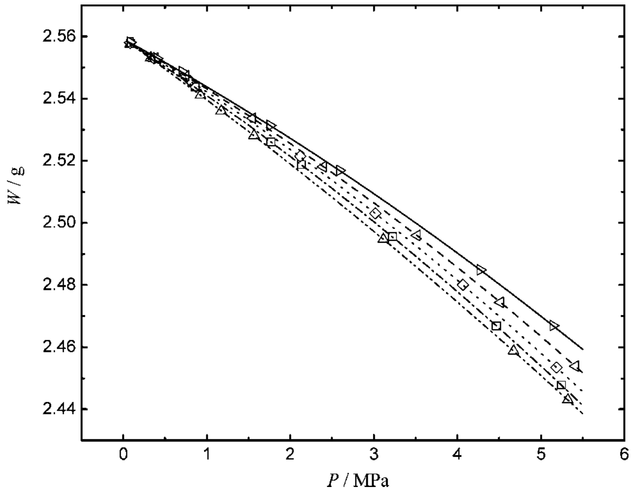

Figure 2. Calibration curves of the empty sample pan from this work: Δ, 303.2 K; □, 313.2 K; ◇, 323.2 K; open triangle pointing left, 333.2 K; open triangle pointing right, 343.2 K; and lines, calculated using eq 1.

Buoyancy Effect Calculations. The correction for buoyancy effect was calculated using a similar approach done by Shiflett and Yokozeki[5] with some simplifications. In this work, only the buoyancy effect on the sample pan (container) and the sample was taken into account, since these are the major contributors of the buoyancy correction.[5] The buoyancy effect on the sample pan was evaluated by calibrating the mass of the sample pan with respect to the changes in temperature and pressure. The sample pan (without sample load) was weighed in a CO_2-filled environment at different temperatures and pressures. Figure 2 shows the calibration curves of the sample pan. As shown in this figure, the mass of the empty sample pan increases as the temperature increases and decreases as the pressure increases. This is a typical observation due to the effect of buoyant force on the sample pan.[5] The results were correlated by an empirical equation of the form

$$m/\mathrm{g} = a_1 + a_2(T/\mathrm{K}) + (a_3 + a_4(T/\mathrm{K}))(P/\mathrm{MPa}) + (a_5 + a_6(T/\mathrm{K}))(P/\mathrm{MPa})^2 \quad (1)$$

where m is the mass of empty pan; T is the system temperature; P is the system pressure; and a_1 to a_6 are empirical constants and were obtained by fitting the calibration data. The values of a_1 to a_6 were 2.310276, $-1.34 \cdot 10^{-4}$, -0.270438, $1.466 \cdot 10^{-3}$, 0.067344, and $-4.18 \cdot 10^{-4}$, respectively. The average absolute percentage deviation (AAD) of the calculated result was $2 \cdot 10^{-4}$. The AAD was defined as

$$\mathrm{AAD} = \frac{\sum_{i=1}^{n} |(\varepsilon_{\mathrm{calcd}} - \varepsilon_{\mathrm{exptl}})/\varepsilon_{\mathrm{exptl}}|_i}{n} \quad (2)$$

where n represents the number of data points; $\varepsilon_{\mathrm{calcd}}$ is the calculated value of the property; and $\varepsilon_{\mathrm{exptl}}$ is the experimental value of the property.

The buoyancy correction on the RTIL sample was evaluated by a similar relation used by Shiflett and Yokozeki[5] as in eq 3

$$B_{IL} = V_{IL}\rho_{CO_2}(T,P) = \frac{m_{IL}}{\rho_{IL}}\rho_{CO_2}(T,P) \quad (3)$$

where B_{IL} is the buoyancy correction on RTIL; V_{IL} is the volume of ionic liquid; m_{IL} is the mass of ionic liquid; ρ_{IL} is the density of ionic liquid; and ρ_{CO_2} is the density of carbon dioxide. To improve the accuracy of the buoyancy correction, we have employed accurate equations for the calculation of density for RTIL and CO_2.

The density of RTIL was estimated using an extended Ye and Shreeve group contribution method equation of state proposed by Gardas and Countinho.[27] This equation of state is a modification of the Ye and Shreeve[28] proposed group additivity method for the estimation of densities of RTILs and salts. The extended Ye and Shreeve group contribution method equation of state has the form as in eq 4

$$\rho_{IL} = \frac{M}{NV_0(b_1 + b_2T + b_3P)} \quad (4)$$

where M is the molecular weight of RTIL; N is Avogadro's constant; V_0 is the molecular volume of RTIL at the reference temperature (T_0) and pressure (P_0) and is assumed as the linear sum of the volumes of cation (V_+) and anion (V_-); whereas the coefficient b_1 is $(1 + \zeta)$; b_2 is the isobaric expansivity, α_P; b_3 is the isothermal compressibility, κ_T; and ζ is equal to $-(\alpha_P T_0 + \kappa_T P_0)$. The cation and anion volumes were obtained from the work of Gardas and Countinho.[27] The coefficients b_i were estimated by fitting eq 4 to available experimental data. For [Bmim][PF_6], a total of 43 data points from 3 cited references[29−31] with temperatures ranging from (298.2 to 353.15) K and pressures up to 202.11 MPa were fitted to determine the coefficients b_i. The values of coefficients b_i obtained were 0.8313, $5.704 \cdot 10^{-4}\ K^{-1}$, and $-2.745 \cdot 10^{-4}\ MPa^{-1}$, respectively. The (AAD) of densities from the experimental densities[29−31] was 0.15 %. For [Emim][BF_4], a total of 96 data points from the work of Gardas et al.[32] for the temperature range of (293.15 to 393.15) K and pressures up to 30 MPa were fitted to obtain the coefficients b_i. The calculated values of coefficients b_i were 0.8152, $5.939 \cdot 10^{-4}\ K^{-1}$, and $-3.742 \cdot 10^{-4}\ MPa^{-1}$, respectively. The AAD of predicted densities from the experimental densities[32] was 0.05 %.

The density of carbon dioxide was calculated using an accurate equation of state for CO_2 presented by Huang et al.[33] The equation was a combination of an analytical part and a nonanalytical part and has the expression as in eq 5

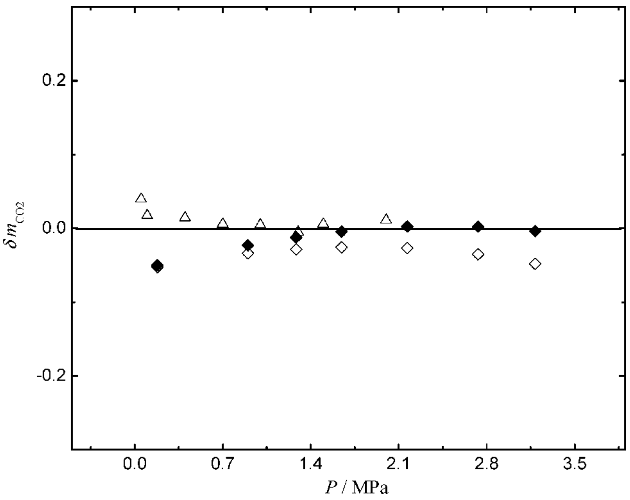

Figure 3. Effect of buoyancy correction on CO_2 solubility in [Bmim][PF_6] at 323 K: ◇, Shiflett and Yokozeki;[5] ◇, this work (without buoyancy correction); ◆, this work (with buoyancy correction).

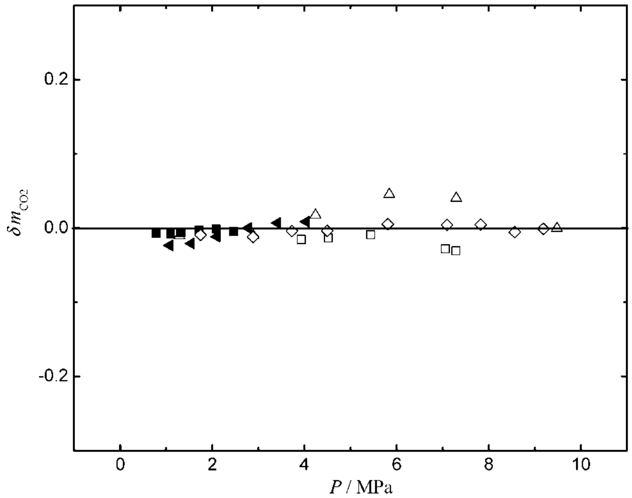

Figure 4. Comparison of CO_2 solubility in [Bmim][PF_6] with literature data: (Δ, 313 K; ◇, 333 K) Perez-Salado Kamps et al.;[34] (□, 313 K) Zhang et al.;[35] (■, 313 K; solid triangle pointing left, 333 K) this work.

Table 1. Solubility of Carbon Dioxide m_{CO2} (with Buoyancy Correction) in [Emim][BF_4]

P/MPa	m_{CO_2}/($mol_{CO_2} \cdot kg_{IL}^{-1}$)
$T = 303.2$ K	
0.496	0.2067
1.035	0.4308
2.068	0.8611
3.112	1.2673
4.155	1.5999
$T = 313.2$ K	
0.503	0.1607
1.040	0.3471
2.068	0.7058
3.136	1.0634
4.207	1.3796
$T = 323.2$ K	
0.503	0.1228
1.049	0.2817
2.118	0.5946
3.136	0.8847
4.254	1.1777
$T = 333.2$ K	
0.503	0.0951
1.049	0.2294
2.118	0.4917
3.186	0.7456
4.329	0.9961
$T = 343.2$ K	
0.517	0.0802
1.058	0.1940
2.167	0.4210
3.236	0.6254
4.329	0.8104

$$Z = P/\rho RT = 1 + c_2\rho' + c_3\rho'^2 + c_4\rho'^3 + c_5\rho'^4 + c_6\rho'^5 c_7\rho'^2 \exp[-d_{21}\rho'^2] + c_8\rho'^4 \exp[-d_{21}\rho'^2] + d_{22}\rho' \exp[-d_{27}(\Delta T)^2] d_{23}\Delta\rho/\rho' \exp[-d_{25}(\Delta\rho)^2 - d_{27}(\Delta T)^2] + d_{24}\Delta\rho/\rho' \exp[-d_{26}(\Delta\rho)^2 - d_{27}(\Delta T)^2] \quad (5)$$

where the reduced temperature and density are $T' = T/T_c$, $\rho' = \rho/\rho_c$, respectively, and $\Delta T = 1 - T'$, $\Delta\rho = 1 - 1/\rho'$, and the parameters are defined in the cited reference.[33] The resulted average deviations in density estimation of Huang et al.[33] were

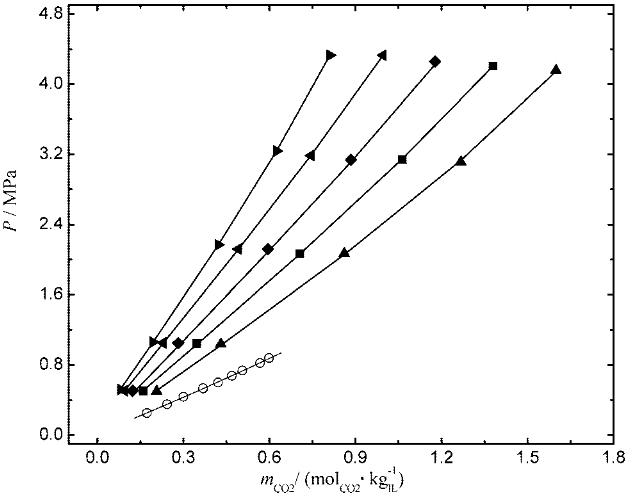

Figure 5. Equilibrium solubility of CO_2 in [Emim][BF_4] at various temperatures: (▲, 303.2 K; ■, 313.2 K; ◆, 323.2 K; solid triangle pointing left, 333.2 K; solid triangle pointing right, 343.2 K), present experimental results; (□, 298.15 K), data of Kim et al.;[14] and solid lines, calculated using eq 6.

Table 2. Henry's Constant of CO_2 in IL at Zero Pressure $k_{H,CO_2}(T)$

T/K	$k_{H,CO_2}(T)$/MPa	l_1	l_2	l_3	(AAD)/%
		[Bmim][PF_6]			
303.2	1.3203	31.0274	−0.03735	−5837.39	0.76
313.2	1.6501				
323.2	2.0514				
333.2	2.4771				
343.2	2.7979				
		[Emim][BF_4]			
303.2	2.3526	22.6903	−0.02116	−4678.71	0.80
313.2	3.0465				
323.2	3.9374				
333.2	4.9923				
343.2	6.0096				

Table 3. Comparison of the Calculated AAD at Various Temperatures between the Data of This Work and the Data of Shiflett and Yokozeki[5]

T/K	no. of data points	(AAD)/%
	Experimental Data of Shiflett and Yokozeki[5]	
283.15	9	5.90
298.15	9	0.22
323.15	9	0.22
348.15	9	0.04
	Experimental Data of this work	
303.2	7	0.05
313.2	7	0.08
323.2	7	0.14
333.2	7	0.14
343.2	7	0.23

0.16 % in the gaseous region, 0.91 % in the critical region, and 0.10 % in the liquid region. This equation was selected since it is considered as the most accurate equation especially on the critical region.

Results and Discussion

The solubility of carbon dioxide in RTILs [Bmim][PF_6] and [Emim][BF_4] were measured at temperatures from (303.2 to 343.2) K and pressures below 5 MPa using a thermogravimetric microbalance.

The effect of buoyancy was accounted for on the evaluation of CO_2 solubility in the investigated RTILs. As reported by Shiflett and Yokozeki,[5] the effect of buoyancy correction was found to be significant at high pressures but negligible near atmospheric pressure. We used the RTIL, [Bmim][PF_6], to show this effect. Figure 3 shows the plot of the deviations (δm_{CO_2}) of the measured CO_2 solubilities (with and without buoyancy correction) and the published data of Shiflett and Yokozeki[5] versus the system pressure. The experimental data from this study without buoyancy correction have lower values than the data of Shiflett and Yokozeki[5] and the experimental data from this work with buoyancy correction. This figure justifies that the effect of buoyancy is significant, as shown by a large deviation on the values of the measured CO_2 solubilities without buoyancy correction. The present experimental data with buoyancy correction was also in good agreement with the measured values of Shiflett and Yokozeki,[5] thus validating the present experimental procedures and apparatus. Hence, from this point hereon, the solubility of CO_2 was evaluated with buoyancy correction.

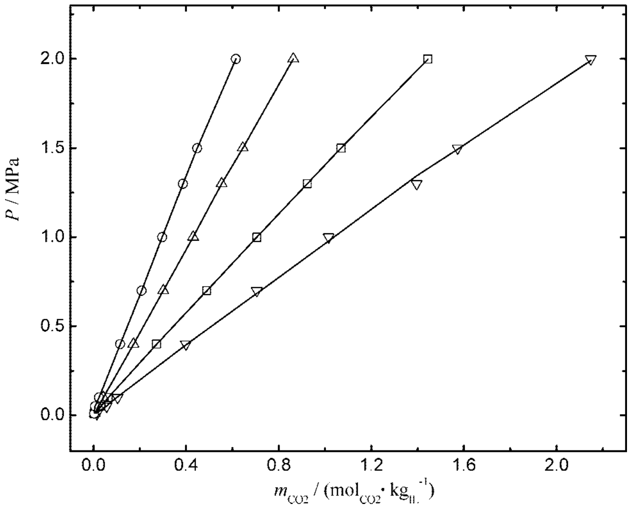

Figure 6. Comparison of the calculated solubility for [Bmim][PF_6], using the determined parameters of this work, with the data of Shiflett and Yokozeki:[5] (▽, 283.15 K; □, 298.15 K; Δ, 323.15 K; ○, 348.15 K) data of Shiflett and Yokozeki;[5] and solid lines, calculated using eq 6 and determined parameters of this work.

Aside from the data of Shiflett and Yokozeki,[5] which was in good agreement with the results from this work, the present measurements of solubility of carbon dioxide in [Bmim][PF_6] were also compared to other available data to further validate the present experimental procedures and apparatus. Figure 4 shows the comparison of the solubility data for [Bmim][PF_6] at (313 and 333) K from this work and available literature data in terms of the deviations (δm_{CO_2}) of the measured data from the calculated values. As shown in this figure, the present experimental data were also in good agreement among the available literature data of Perez-Salado Kamps et al.[34] and Zhang et al.,[35] as shown by acceptable deviations, hence validating further the present experimental procedures and apparatus.

To discuss the effect of temperature and pressure on the solubility data, the present solubility measurements of [Emim][BF_4] (see also Table 1) at the studied isotherms are plotted and shown in Figure 5. [Emim][BF_4] was used as the representative system to show the effect of temperature and pressure on the solubility data since the studied RTILs behave similarly. As shown in Figure 5, the solubility increases with increasing pressure and decreases with increasing temperature.

Carbon Dioxide Solubility Modeling. Since RTILs have negligible vapor pressure, the gaseous phase is assumed to consist of pure CO_2, and the vapor−liquid equilibrium condition results in the extended Henry's law for CO_2 and is written as

$$k_{\mathrm{H,CO_2}}(T,P)a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}}) = f_{\mathrm{CO_2}}(T,P) \tag{6}$$

where $k_{\mathrm{H,CO_2}}(T,P)$ is Henry's constant of CO_2 in RTIL (based on molality scale), $a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}})$ is the activity of CO_2 in the liquid (the influence of pressure on the activity is neglected), and $f_{\mathrm{CO_2}}(T,P)$ is the fugacity of CO_2 in the vapor phase.

The Henry's constant of CO_2 in IL $k_{\mathrm{H,CO_2}}(T,P)$ is expressed as

$$k_{\mathrm{H,CO_2}}(T,P) = k_{\mathrm{H,CO_2}}(T)\exp\left(\frac{\bar{V}^{\infty}_{\mathrm{m,CO_2}}P}{RT}\right) \tag{7}$$

where $k_{\mathrm{H,CO_2}}(T)$ is Henry's constant of CO_2 in RTIL at zero pressure; $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ is the partial molar volume of CO_2 at infinite dilution in RTIL; P is the system pressure; T is the system temperature; and R is the gas constant.

The activity of CO_2 in RTIL (on molality scale) $a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}})$ is represented as

$$a_{\mathrm{CO_2}}(T,m_{\mathrm{CO_2}}) = \frac{m_{\mathrm{CO_2}}}{m^{\mathrm{o}}}\gamma^{*}_{\mathrm{CO_2}} \tag{8}$$

where $m_{\mathrm{CO_2}}$ is the solubility of CO_2 in RTIL (on molality scale); m^{o} is the reference solubility (1 $\mathrm{mol\cdot kg^{-1}}$); and $\gamma^{*}_{\mathrm{CO_2}}$ is the activity coefficient of CO_2, which is calculated from the virial expansion proposed by Pitzer[36] to describe the excess Gibbs energy of an aqueous solution and is given as

$$\ln\gamma^{*}_{\mathrm{CO_2}} = 2\frac{m_{\mathrm{CO_2}}}{m^{\mathrm{o}}}\beta^{(0)}_{\mathrm{CO_2,IL}} + 3\left(\frac{m_{\mathrm{CO_2}}}{m^{\mathrm{o}}}\right)^{2}\tau^{(0)}_{\mathrm{CO_2,CO_2,IL}} \tag{9}$$

where the parameters $\beta^{(0)}_{\mathrm{CO_2,IL}}$ and $\tau_{\mathrm{CO_2,CO_2,IL}}{}^{(0)}$ describe the binary and ternary interactions between CO_2 molecules in RTIL, respectively.

The fugacity of pure CO_2 at equilibrium temperature and pressure $f_{\mathrm{CO_2}}(T,P)$ was calculated from the equation of state of Huang et al.[33] The expression for the fugacity has the following form

$$\begin{aligned}\ln f_{\mathrm{CO_2}} = {} & (Z-1) + \ln(\rho RT) + c_2\rho' + \frac{1}{2}c_3\rho'^2 + \frac{1}{3}c_4\rho'^3 + \\ & \frac{1}{4}c_5\rho'^4 + \frac{1}{5}c_6\rho'^5 + \frac{1}{2d_{21}}c_7\{1-\exp(-d_{21}\rho'^2)\} + \\ & \frac{1}{2d_{21}^2}c_8\{1-(1+d_{21}\rho'^2)\exp(-d_{21}\rho'^2)\} + \\ & d_{22}\rho'\exp[-d_{27}(\Delta T)^2] - \frac{d_{23}}{2d_{25}}\exp\{-d_{25}(\Delta\rho)^2 - \\ & d_{27}(\Delta T)^2\} - \frac{d_{24}}{2d_{26}}\exp\{-d_{26}(\Delta\rho)^2 - d_{27}(\Delta T)^2\}\end{aligned} \tag{10}$$

where $f_{\mathrm{CO_2}}$ is the fugacity of CO_2 at the system temperature and pressure; Z is the compressibility factor; ρ is the density of CO_2; and the other parameters were defined as in eq 5.

The Henry's constant of CO_2 in RTIL at zero pressure $k_{\mathrm{H,CO_2}}(T)$ was obtained by extrapolating (at preset temperature) the present experimental results for the solubility pressure of CO_2 in RTIL using linear regression, and the results were presented in Table 2.

$$k_{\mathrm{H,CO_2}}(T) = \lim_{P\to 0}\left[\frac{f_{\mathrm{CO_2}}(T,P)}{m_{\mathrm{CO_2}}/m^{\mathrm{o}}}\right] \tag{11}$$

The final results for $k_{\mathrm{H,CO_2}}(T)$ as a function of temperature were correlated by relations as in eq 12

$$\ln(k_{\mathrm{H,CO_2}}/\mathrm{MPa}) = l_1 + l_2(T/\mathrm{K}) + l_3/(T/\mathrm{K}) \tag{12}$$

where $k_{\mathrm{H,CO_2}}$ is the Henry's law constant at zero pressure and T is the absolute temperature. Using eq 12, the parameters l_i were determined by fitting the obtained extrapolated $k_{\mathrm{H,CO_2}}(T)$, and the results were also presented and shown in Table 2. The determined parameters l_i correlated well the obtained $k_{\mathrm{H,CO_2}}(T)$ as a function of temperature as justified by AAD of about 0.8 % for each studied RTIL.

The new solubility pressure data for the studied systems (CO_2 + RTIL) can be described through $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and the interaction parameters $\beta^{(0)}_{\mathrm{CO_2,IL}}$ and $\tau^{(0)}_{\mathrm{CO_2,CO_2,IL}}$. However, $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ turned out to be sufficient to describe the experimental total pressures with an overall AAD of 0.43 % using the experimental results of this work. The partial molar volume of CO_2 at infinite dilution in RTIL $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ was expressed as a function of temperature and is given as

$$\bar{V}^{\infty}_{\mathrm{m,CO_2}}/\mathrm{m^3\cdot mol^{-1}} = n_1 + n_2(T/\mathrm{K}) \tag{13}$$

The obtained parameters n_i were as follows: [Bmim][PF_6] (428.15 and −1.458 for n_1 and n_2, respectively); and [Emim][BF_4] (2226.10 and −6.710 for n_1 and n_2, respectively). The binary interaction parameter $\beta^{(0)}_{\mathrm{CO_2,IL}}$ has regressed values of 0.04381 and −0.14019 for [Bmim][PF_6] and [Emim][BF_4], respectively.

Application of the Model to Literature Data. The determined parameters $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ of this work were applied to the calculation of the solubility of CO_2 in [Bmim][PF_6] for the data of Shiflett and Yokozeki.[5] The results of calculations at various temperatures for the data of Shiflett and Yokozeki[5] are presented in Table 3. Figure 6 shows the correlated data of Shiflett and Yokozeki[5] using the determined parameters of this study. As shown in this figure, the correlation from this work was successfully applied to sets of data of Shiflett and Yokozeki,[5] and for having an overall AAD of about 1.59 %, the determined parameters $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ correlated well their data. Similarly, as shown in Figure 5, the determined parameters $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ of this work were also applied to the calculation of the solubility of CO_2 in [Emim][BF_4] for the data of Kim et al.[14] The determined parameters $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ of this work for [Emim][BF_4] also represented well the data of Kim et al.,[14] as shown in Figure 5 and by having an overall AAD of about 0.02 %. Within the pressure range under consideration, the present determined parameters $\bar{V}^{\infty}_{\mathrm{m,CO_2}}$ and $\beta^{(0)}_{\mathrm{CO_2,IL}}$ for the studied RTILs successfully predicted also the solubility data from the literature, thus validating the applicability of the correlation.

Conclusions

Carbon dioxide solubilities in both ionic liquids, [Bmim][PF_6] and [Emim][BF_4], were measured at various temperatures of (303.2, 313.2, 323.2, 333.2, and 343.2) K and pressures below 5 MPa. Highly accurate equations of states were used in the density calculations for both ionic liquid and carbon dioxide to account for the buoyancy effect. The said effect was found to be significant at high pressures and cannot be neglected. An extended Henry's law correlation was used to represent the obtained experimental results, which is quite satisfactory, as shown by an overall AAD of 0.43 %. The correlation has also been applied to the selected literature values, and the predicted results were also satisfactory as shown by the overall AAD of (1.59 and 0.02) % for [Bmim][PF_6] and [Emim][BF_4], respectively.

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