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Solubilities of CO_2 in 1-Butyl-3-methylimidazolium Hexafluorophosphate and 1,1,3,3-Tetramethylguanidium Lactate at Elevated Pressures

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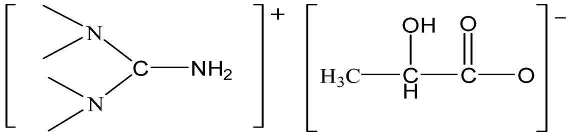
The solubilities of CO_2 in 1-butyl-3-methylimidazolium hexafluorophosphate and 1,1,3,3-tetramethylguanidium lactate at the temperatures ranging from (297 to 328) K and the pressures ranging from (0 to 11) MPa were determined. The extended Henry's law was applied to correlate the solubility data, and the thermodynamic properties such as standard enthalpy, standard Gibbs free energy, standard entropy, and standard heat capacity of these two systems were obtained. Experimental results showed that the solubilities of CO_2 in TMGL are slightly higher than those in [bmim][PF_6].

Introduction

In the industrial process of CO_2 absorption, the volatile solvents such as aqueous amines have been used for capturing CO_2, which causes environmental problems. Therefore, a nonvolatile solvent that could facilitate the sequestration of CO_2 without loss of the solvent into the gas stream could be advantageous.

Ionic liquids (ILs) have attracted extensive interest in recent years as being environmentally benign solvents for various chemical reactions[1−4] and processes engineering[5,6] due to their favorable properties,[7−9] such as nonflammability and negligible vapor pressure. There are possible advantages in using ILs for absorbing CO_2. To develop a new process for absorption of CO_2, it is important to have the knowledge of solubility of CO_2 in ILs. Experimental data on the solubility of CO_2 in imidazolium ILs have been reported in the literature,[10−15,21] where the solubility of CO_2 in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) is generally larger than [C_8mim][BF_4], [bmim][NO_3], [C_8mim][PF_6], [Nbupy][BF_4], and [emim][$EtSO_4$].[10] Recently, Gao et al.[16] reported a new ionic liquid 1,1,3,3-tetramethyl-guanidium lactate (TMGL) and used it for the absorption of SO_2.[17] Considering that TMGL may be the potential solvent for absorption of CO_2, we determined the solubility of CO_2 in [bmim][PF_6] and TMGL in this work. The structure of TMGL is as shown below.



The solubilities of CO_2 in TMGL and [bmim][PF_6] were determined at temperatures ranging from (297 to 328) K and at pressures ranging from (0 to 11) MPa. The solubility data were correlated by means of an extended Henry's law, and the thermodynamic properties were obtained. The results showed that the solubility of CO_2 in TMGL is slightly higher than in [bmim][PF_6].

Experimental Section

Chemicals. CO_2 was purchased from Beijing Analytical Instrument Factory with a purity of 99.95 %. 1,1,3,3-Tetramethylguanidium lactate (TMGL) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were synthesized according to the literature.[15,18] The materials necessary for the synthesis of the ILs include *N*-methylimidazole (Zhejiang KaiLe Chemical Factory, 98 %, distilled over KOH under vacuum), butyl bromide (99.5 %, Chemical Reagent Co. of Chinese Military Academy of Science), potassium fluorophosphate (>99 %, Tianjin Chemical Academy of Research and Designing), 1,1,3,3-tetramethylguanidine (>99 %, Fluka), and DL-lactic acid (95 %, Acros, distilled over KOH under vacuum). The synthesized TMGL sample was dried under vacuum at 373 K for 24 h before use. The synthesized [bmim][PF_6] sample was dried under vacuum at 343 K for 48 h because [bmim][PF_6] can decompose at high temperature.[12] The water content of ILs after drying was less than 200 ppm as measured by 787 KF Titrino.

The synthesized ILs were characterized by ^1H NMR spectrum measured on a Bruker AM 400 MHz spectrometer, using D_2O and $CDCl_3$ as solvent with TMS as internal standard. FT-IR spectrums were taken by a Perkin-Elmer IR spectrometer, using a NaCl disk. All these results are as follows:

TMGL: ^1H NMR (400 MHz, D_2O) 1.30 (d, 3H), 2.95 (s, 12H), 4.17 (q, 1H). IR 3203, 2970, 1606, 1571, 1410 cm^{-1}.

[bmim][PF_6]: ^1H NMR (400 MHz, $CDCl_3$) 1.17 (t, 6H), 1.49 (s, 4H), 2.03 (m, 4H), 4.29 (t, 3H), 4.48 (t, 2H), 7.43 (t, 1H), 7.59 (t, 1H), 8.47 (s, 1H). IR 3159, 3091, 1960, 1881, 1566, 1459 cm^{-1}.

Comparing the data of ^1H NMR of our samples with those reported by Wu et al.[19] and Gao et al.[16] respectively, it is found that the agreement is good. The purity of [bmim][PF_6] is 98.8 %, and that of TMGL is 98.2 %. The residual bromine content of [bmim][PF_6] was less than 50 ppm as

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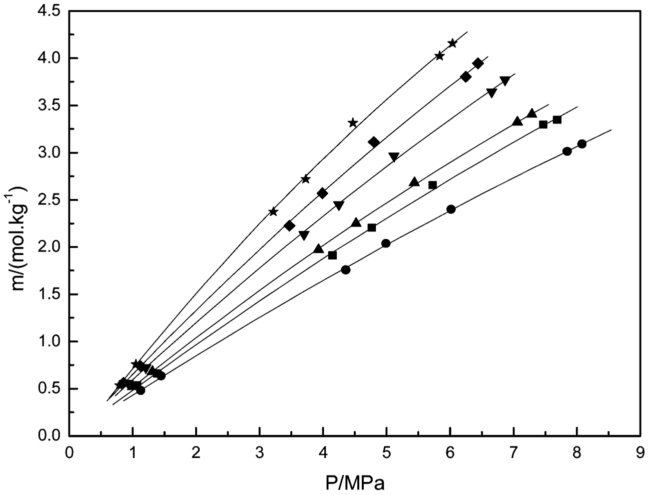

Figure 1. Solubilities of CO_2 in [bmim][PF_6]: *, 297.56K; ×, 304.38K; ▼, 308.60K; ▲, 314.25K; ■, 319.06K; ●,322.52K; —, correlation.

Table 1. Solubilities of CO_2 in [bmim][PF_6] at Different Pressures and Temperatures

$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$	$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$	$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$
T = 297.56 K		T = 304.38 K		T = 308.60 K	
0.79	0.536	0.86	0.564	0.93	0.560
1.05	0.758	1.13	0.739	1.21	0.723
3.22	2.372	3.47	2.227	3.70	2.136
3.73	2.718	3.99	2.570	4.25	2.451
4.47	3.314	4.80	3.113	5.12	2.965
5.84	4.022	6.25	3.802	6.66	3.644
6.04	4.156	6.44	3.944	6.87	3.769
T = 314.25 K		T = 319.06 K		T = 322.52 K	
1.00	0.522	1.07	0.537	1.13	0.479
1.31	0.680	1.39	0.661	1.45	0.634
3.93	1.970	4.15	1.909	4.36	1.755
4.52	2.250	4.77	2.203	4.99	2.037
5.44	2.681	5.73	2.652	6.02	2.398
7.06	3.320	7.47	3.295	7.85	3.013
7.29	3.406	7.69	3.346	8.08	3.091

determined by adding 0.5 mL of 0.01mol/L $AgNO_3$ solution to 10 g of [bmim][PF_6].

Solubility Measurement. The apparatus mainly consisted of a high-pressure stainless steel cell and a gas storage tank. They were placed in a water bath. The high-pressure cell had a volume scale window through which the height of ILs could be read. In the high-pressure cell there was a magnetic rotor that could accelerate the equilibrium. There was a pressure sensor placed between the cell and the tank through which the pressure of gas–liquid system could be obtained.

Predetermined amounts of the ionic liquid weighed by an electronic balance were loaded in the high-pressure cell and degassed for 12 h, an accurate mass of CO_2 was pressed into the storage tank using a high-pressure pump, and the water bath was controlled at the desired temperature with a temperature uncertainty of ± 0.1 K. As the gas entered into the solubility cell, it was absorbed in the ionic liquid, and the pressure decreased gradually. When the pressure was invariable for 2 h, the equilibrium can be considered having been reached, then the pressure of CO_2 and the height of the ionic liquid were recorded, and the solubility of CO_2 in the ionic liquid was determined.

Masses of the solute and solvent were obtained using an electronic balance with uncertainty of ± 0.0001 g. Uncertainty of the pressure was ± 0.25 %. The height of the ILs was read from a ruler with an uncertainty of ± 0.0005 m. Calculated by error transferring method, the estimated uncertainty of the solubility measurement is ± 0.8 %.

Modeling

The gaseous phase is assumed to be pure CO_2 due to the negligible vapor pressure of ILs. Applying the extended Henry's laws equation to CO_2 as follows: [12]

$$H_{CO_2}(T,P)a_{CO_2}(T,m_{CO_2}) = f_{CO_2}(T,P) \qquad (1)$$

in which $H_{CO_2}(T,P)$ is the Henry's law constant of CO_2 in ILs based on the molality scale, $a_{CO_2}(T,m_{CO_2})$ is the activity of CO_2 in the liquid, and $f_{CO_2}(T,P)$ is the fugacity of CO_2 at the equilibrium temperature and pressure. They can be expressed as:

$$H_{CO_2}(T,P) = H_{CO_2}(T)\exp\left(\frac{V_{CO_2}{}^{\infty}P}{RT}\right) \qquad (2)$$

$$a_{CO_2} = \frac{m_{CO_2}}{m^{\circ}}\gamma_{CO_2}{}^{*} \qquad (3)$$

$$f_{CO_2}(T,P) = P\phi_{CO_2}(T,P) \qquad (4)$$

where $H_{CO_2}(T)$ is the Henry's law constant at the vapor pressure of the solvent (P_{IL}^{sat}), $V_{CO_2}^{\infty}$ is the partial molar volume of CO_2 at infinite dilution, m° = 1 mol·kg^{-1}, $\gamma_{CO_2}{}^{*}$ is the activity coefficient of CO_2, and ϕ is the fugacity coefficient.

The fugacity coefficient (ϕ) can be calculated using the SRK equation of state,[20] and the Henry's constant of CO_2 can be evaluated from the experimental data according to the following equation:

$$H_{CO_2}(T) = \lim_{P \to P_{IL}^{S}=0}\left[\frac{f_{CO_2}(T,P)}{m_{CO_2}/m^{\circ}}\right] \qquad (5)$$

Thermodynamic properties of solutions of CO_2 in ILs related to the Henry's constant can be calculated as follows:

$$\Delta_{sol}G = RT\ln(H(T,P)/P^{\circ}) \qquad (6)$$

$$\Delta_{sol}H = R\left(\frac{\partial\ln(H(T,P)/P^{\circ})}{\partial(1/T)}\right)_P \qquad (7)$$

$$\Delta_{sol}S = (\Delta_{sol}H - \Delta_{sol}G)/T \qquad (8)$$

$$\Delta_{sol}C_p = \left(\frac{\partial\Delta_{sol}H}{\partial T}\right)_P \qquad (9)$$

in which $\Delta_{sol}G^{\circ}$, $\Delta_{sol}H^{\circ}$, $\Delta_{sol}S^{\circ}$, and $\Delta_{sol}C_p{}^{\circ}$ is the standard Gibbs free energy, standard enthalpy, standard entropy, and standard heat capacity of these two systems, respectively, where the standard state represents the state of P = 0.1 MPa and T = 298.15 K.

Results and Discussions

The solubilities of CO_2 in [bmim][PF_6] measured up to a pressure of 8.08 MPa at six temperatures from (297 to 323) K were presented in Table 1 and Figure 1. In Figure 2, the ratio of CO_2 fugacity to the molality of CO_2 were plotted versus the total pressure, from which Henry's constants of CO_2 in [bmim][PF_6] were obtained and listed in Table 3. Thermodynamics properties of CO_2 in [bmim][PF_6]

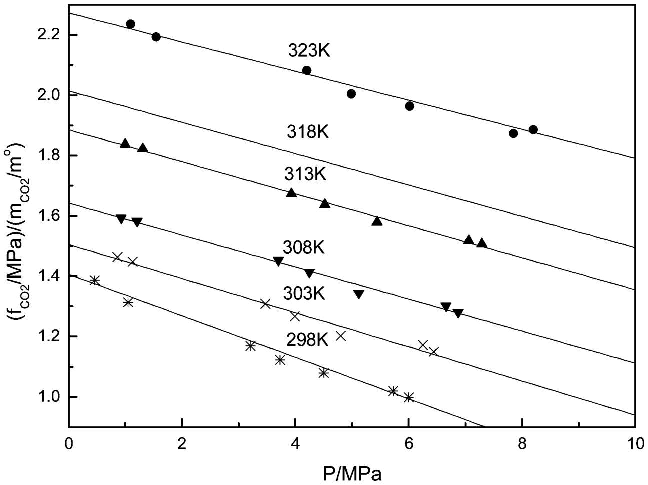

Figure 2. Influence of the total pressure on the ratio of CO_2 fugacity to CO_2 molality in [bmim][PF_6]: *, 297.56K; ×, 304.38K; ▼, 308.60K; ▲, 314.25K; ■, 319.06K; ●,322.52K; −, correlation.

Table 2. Solubilities of CO_2 in TMGL at Different Pressures and Temperatures

P/MPa	m_{CO_2}/mol·kg^{-1}	P/MPa	m_{CO_2}/mol·kg^{-1}	P/MPa	m_{CO_2}/mol·kg^{-1}
T = 308.05 K		T = 319.30 K		T = 327.46 K	
0.49	0.286	0.73	0.411	1.24	0.617
0.93	0.561	1.02	0.553	1.11	0.537
2.24	1.514	2.51	1.320	2.77	1.141
2.78	1.829	3.14	1.635	3.55	1.362
3.33	2.229	3.73	1.923	4.16	1.593
5.09	3.071	5.73	2.767	6.24	2.249
7.19	4.077	7.99	3.436	8.74	2.913
7.76	4.218	8.65	3.659	9.57	3.056
8.33	4.392	9.25	3.723	10.18	3.239

Table 3. Henry's Constants of CO_2 in Ionic Liquids at Different Temperatures

T/K	H_{CO_2}/MPa	T/K	H_{CO_2}/MPa
[bmim][PF_6]		TMGL	
323	2.27	328	2.36
318	2.01	318	1.79
313	1.89	308	1.46
308	1.64		
303	1.51		
298	1.41		

Table 4. Thermodynamic Properties of Solutions for CO_2 in Ionic Liquids at the Standard State

solutions	$\Delta_{sol}G°$/kJ·mol^{-1}	$\Delta_{sol}H°$/kJ·mol^{-1}	$\Delta_{sol}S°$/J·mol^{-1}·K^{-1}	$\Delta_{sol}C_p°$/J·mol^{-1}·K^{-1}
CO_2 + [bmim][PF_6] (exp)	6.54	−15.66	−79.47	69.52
CO_2 + [bmim][PF_6] (lit[12])	6.46	−17.24	−79.5	63.2
CO_2 + TMGL	5.59	−20.13	−86.30	82.53

calculated from the correlation of the Henry's constant were presented in Table 4.

In Figure 3, the measured solubility data of CO_2 in [bmim][PF_6] at 314.25K were compared with the literature data at 313 K reported by Kamps et al.,[12] Liu et al.,[21] and Aki et al.[22] It can be found that the solubility data from (0 to 5) MPa are all in good agreement, while the discrepancies among them becomes larger at high pressure region, it is probably due to the operation difficulties at elevated pressures. Our measured data have the similar tendency to those of Kamps et al.,[12] Liu et al.,[21] and Aki et al.,[22] and more close to the data of Kamps et al.[12] Considering our

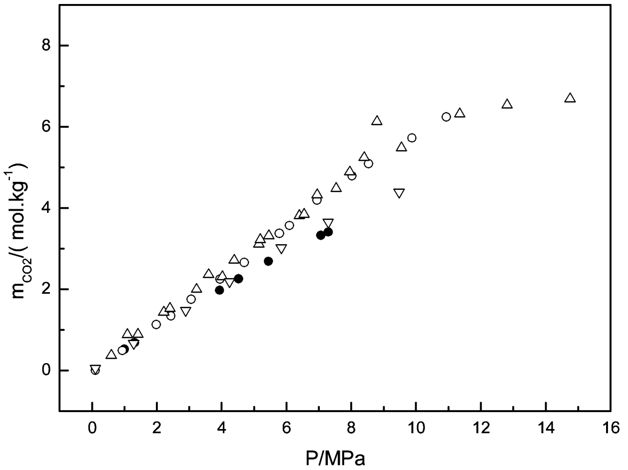

Figure 3. Comparison of the solubilities of CO_2 in [bmim][PF_6]: ●, this work (314.25 K); △, Kamps et al.[12] (313 K); ○, Liu et al.[21] (313 K); ▽, Aki et al.[22] (313 K).

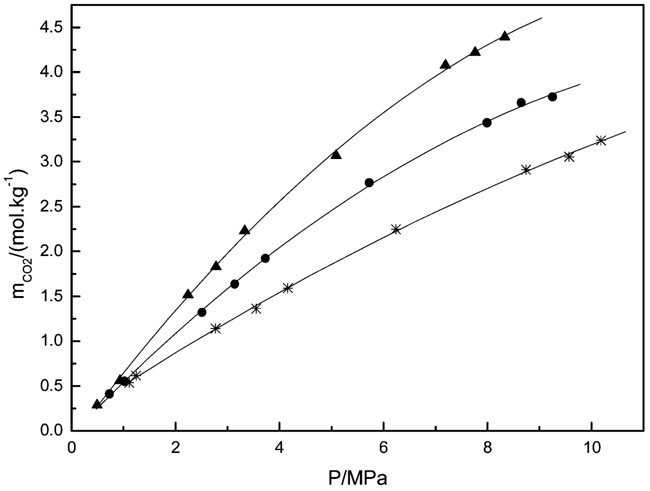

Figure 4. Solubilities of CO_2 in TMGL: ▲, 308.05 K; ●, 319.30 K; *, 327.46 K; −, correlation.

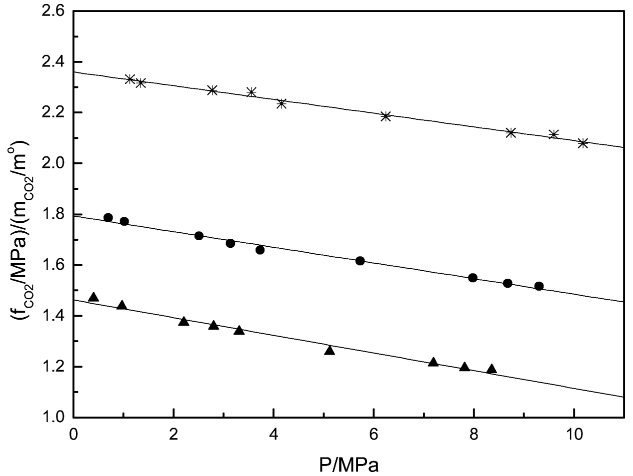

Figure 5. Influence of the total pressure on the ratio of CO_2 fugacity to CO_2 molality in TMGL: ▲, 308.05 K; ●, 319.30 K; *, 327.46 K; −, correlation.

determination operated at high-temperature comparing to that of Kamps et al.,[12] our measured data are slightly smaller than those of Kamps et al.[12] The Henry's constants of CO_2 in [bmim][PF_6] at 313 K was 1.89 MPa in this work, which is the same as the value reported by Kamps et al.[12] Thermodynamics properties of CO_2 in [bmim][PF_6] were also in good agreement with those of Kamps et al.[12] All the measurements of our experiments have been repeated three times, the consistency and accuracy have been systematically calculated, and considering that the experiments were carried out at elevated pressures, our determination are reasonable.

Wu et al.[17] had measured only one solubility of CO_2 in TMGL, which was 0.25 wt %; however, the operating temperature and pressure were not given. In this work, the solubility data of CO_2 in TMGL measured up to a pressure of 10.18 MPa at three temperatures from (308 to 328) K are presented in Table 2 and Figure 4. Henry's constants of CO_2 in TMGL obtained from Figure 5 are presented in Table 3. Thermodynamics properties of solution (CO_2 in TMGL) are presented in Table 4.

By comparing the solubility of CO_2 in [bmim][PF_6] with that in TMGL, we can see that the solubility of CO_2 in TMGL is slightly larger than in [bmim][PF_6], for example, the solubility of CO_2 in [bmim][PF_6] at 319 K and 5.73 MPa is 2.65 $mol{\cdot}kg^{-1}$ while in TMGL is 2.77 $mol{\cdot}kg^{-1}$. As a low-cost and easily prepared ionic liquid, TMGL is somewhat better than [bmim][PF_6] in absorbing CO_2. While compared with aqueous amine, it cannot be used to capture CO_2 in industry due to its limited solvency. More effective ionic liquids for capturing CO_2 are expected to be researched in future.

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