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Solubility of CO_2 in Sulfonate Ionic Liquids at High Pressure

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In this work, the solubility of CO_2 in sulfonate ionic liquids (ILs), such as trihexyl (tetradecyl) phosphonium dodecylbenzenesulfonates ($[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$) and trihexyl (tetradecyl) phosphonium mesylate ($[P_{6,6,6,14}][MeSO_3]$), was determined at temperatures ranging from (305 to 325) K and pressures ranging from (4 to 9) MPa. It was found that the difference of the solubility of CO_2 in two kinds of sulfonate ILs is not dramatic on the basis of molality. The solubility of CO_2 in $[P_{6,6,6,14}][MeSO_3]$ is higher than that in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$. The solubility data were correlated by means of the extended Henry's law, and the thermodynamic functions, such as the standard enthalpy, standard Gibbs free energy, and standard entropy, were obtained. The Henry's law constant for CO_2 in all the investigated ionic liquids increases with increasing temperature.

Introduction

The utilization of green solvents is an effective way to prevent volatile organic compound (VOC) pollution. Recently, ionic liquids (ILs) have attracted much attention due to their unique properties;[1] for example, they have an extremely low vapor pressure, are nonflammable, have excellent solvent power for organic and inorganic compounds, and are easily modified structurally to elicit desired physical properties.[2−4] They have been commonly recognized as a versatile alternative to conventional organic solvents. On the other hand, supercritical carbon dioxide ($scCO_2$) is well-known to be a green solvent, too. Many unique properties have been found by combining the advantages of these two classes of green solvents. Although CO_2 is extremely soluble in ILs, the reverse is not the case. Usually no appreciable ILs solubilized in the CO_2 phase. This constitutes a green system for the extraction of a wide variety of solutes from IL phases without any contamination, which has shown great potential applications in many practical processes and product engineering.[5]

Studies on the binary mixtures of $scCO_2$ and ILs are an interesting and important topic. Much research work has been focused on imidazolium ILs.[6−16] Blanchard et al.[6] studied the extraction of naphthalene from ILs by $scCO_2$ and found that not only was the organic substance extracted efficiently by $scCO_2$ without any IL contamination, but also the IL was recovered in its original purity after extraction and depressurization. Najdanovic-Visak et al.[7] investigated the equilibrium behavior of ILs, water, and ethanol mixtures by adding CO_2. Blanchard et al.[3] and Anthony et al.[8] studied the solubility of CO_2, CH_4, water, and other gases in imidazolium-based ILs and the phase behavior of ILs, water, and CO_2. These studies, although very limited, provide fundamental knowledge for developing reactions and separation technologies by utilizing the unique properties of both ILs and $scCO_2$.[12−16] Recently, a new kind of ILs, sulfonate ILs, has been synthesized.[17,18] Such sulfonate ILs do not contain halides, are more stable with thermal treatment and water, and can be synthesized easily from inexpensive raw materials. Therefore, they are more attractive compared to imidazolium ILs. To our knowledge, there is no reported work on the solubility of CO_2 in sulfonate ILs.

In this paper, the solubility data of CO_2 in sulfonate ILs, such as trihexyl (tetradecyl) phosphonium dodecylbenzenesulfonates ($[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$) and trihexyl (tetradecyl) phosphonium mesylate ($[P_{6,6,6,14}][MeSO_3]$), at temperatures ranging from (305 to 325) K and pressures ranging from (4 to 9) MPa were presented. The effects of temperature and pressure on the solubility of CO_2 were discussed. The measured data were correlated by the extended Henry's law. The thermodynamic properties of IL−CO_2 systems, such as the standard enthalpy, standard Gibbs free energy, and standard entropy, were obtained.

Experimental Section

Synthesis of ILs. The sulfonate ILs ($[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$ and $[P_{6,6,6,14}][MeSO_3]$) were synthesized according to the literature.[17] The decomposition temperatures are 417.8 °C and 383.3 °C for $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$ and $[P_{6,6,6,14}][MeSO_3]$, respectively, which were determined by the thermogravimetric analysis (TGA) method. The synthesized ILs were dried under vacuum at 120 °C for 24 h before use. The water content of ILs after drying was measured by Karl Fischer titration and was <0.1 wt %. The residual chloride in the ILs was 0.002 $mol \cdot L^{-1}$, which was determined by the method reported by Seddon et al.[19] CO_2 was purchased from Beijing Analytical Instrument Factory with a purity of 99.995%.

Solubility Measurements. The apparatus used for CO_2 solubility measurements consists of a high-pressure stainless steel cell with a volume scale window, a gas storage tank, a pressure gauge, a magnetic stirrer, and a temperature-constant water bath; a schematic diagram of the experimental apparatus is shown in Figure 1. The measurement of solubility was carried out by the gravimetric method. An accurate amount of ILs was loaded in the high-

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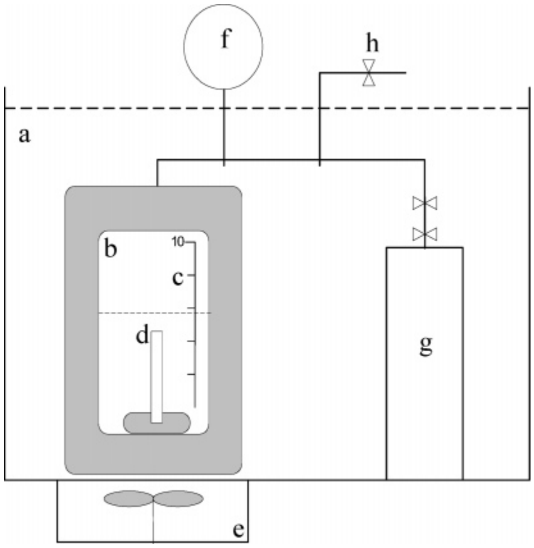

Figure 1. Schematic diagram of the experimental apparatus: a, water bath; b, high-pressure cell; c, volume scale; d, magnetic stirring bar; e, magnetic stirrer; f, pressure gauge; g, gas storage tank; h, needle valve.

pressure cell and degassed for 12 h in the temperature-constant water bath. Then, a fixed mass amount of CO_2 was added to the storage tank and a small Teflon-coated magnetic bar was used for stirring. The equilibrium condition was judged when the pressure was unchanged for ~90 min. After equilibrium was reached, the amount of CO_2 in the gas storage tank was measured with an analytical balance with an accuracy of ±0.001 g and the amount of CO_2 in the gaseous phase could be calculated. Then, the CO_2 dissolved in the ILs could be obtained by the difference. Temperature was measured by a thermometer with an accuracy of better than ±0.01 K and pressure by a pressure transducer (Foxboro/ICT model 93) with an accuracy of ±0.025 MPa. The estimated uncertainty of the solubility is ±0.8%.

Modeling. Due to the negligible vapor pressure of ILs,[3,4] the gaseous phase is assumed to be pure CO_2. Applying the vapor−liquid equilibrium condition to CO_2 results in the extended Henry's law equation:

$$K_{H,CO_2}(T, P)a_{CO_2}(T, m_{CO_2}) = f_{CO_2}(T, P) \tag{1}$$

$K_{H,CO_2}(T, P)$ is the Henry's law constant of CO_2 in ILs based on the molality scale. It is expressed as

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

where $K_{H,CO_2}(T)$ is the Henry's law constant at the vapor pressure of the solvent (P_{IL}^{sat}) and $V_{CO_2}^{\infty}$ is the partial molar volume of the gas at infinite dilution.

$a_{CO_2}(T, m_{CO_2})$ is the activity of CO_2 in the liquid:

$$a_{CO_2} = \frac{m_{CO_2}}{m^\circ}\gamma_{CO_2}^{*} \tag{3}$$

where $m^\circ = 1$ mol·kg^{-1} and $\gamma_{CO_2}^{*}$ is the activity coefficient of CO_2.

The fugacity of CO_2 at the equilibrium temperature and pressure ($f_{CO_2}(T, P)$) is calculated from the following equation

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

where ϕ is the fugacity coefficient, which can be obtained by the use of SRK EOS,[20]

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \tag{5}$$

$$\ln \phi = Z - 1 - \ln\left[Z\left(1 - \frac{b}{V}\right)\right] - \frac{a\alpha}{bRT}\ln\left(1 + \frac{b}{V}\right) \tag{6}$$

where

$$a = a_c\alpha(T) \tag{7}$$

$$b = 0.086\,64RT_c/P_c \tag{8}$$

and

$$a_c = 0.427\,48R^2T_c^2/P_c^2 \tag{9}$$

$$\alpha(T)^{1/2} = 1 + (0.485\,08 + 1.551\,71\omega - 0.156\,13\omega^2)(1 - T_r^{1/2}) \tag{10}$$

where P is the pressure, R is the gas constant, T is the temperature, a and b are the EOS constants, V is the molar volume, T_c is the critical temperature, P_c is the critical pressure, T_r is the reduced temperature, $\alpha(T)$ expresses the temperature dependence of the parameter a, ω is the acentric factor, and Z is the compressibility factor.

The Henry's law constant of CO_2 can be calculated from the vapor−liquid equilibrium (VLE) data according to eq 11.

$$K_{H,CO_2}(T) = \lim_{P \to P_{IL}^{S}=0}\left[\frac{f_{CO_2}(T, P)}{m_{CO_2}/m^\circ}\right] \tag{11}$$

The thermodynamic properties of the system are related to the Henry's law constant by eqs 12−15.

$$\Delta_{sol}G = RT\ln(K_H(T, P)/P^\circ) \tag{12}$$

$$\Delta_{sol}H = R\left(\frac{\partial \ln(K_H(T, P)/P^\circ)}{\partial(1/T)}\right)_P \tag{13}$$

$$\Delta_{sol}S = (\Delta_{sol}H - \Delta_{sol}G)/T \tag{14}$$

$$\Delta_{sol}C_P = \left(\frac{\partial\Delta_{sol}H}{\partial T}\right)_P \tag{15}$$

Results and Discussion

The solubility of CO_2 in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$ and $[P_{6,6,6,14}][MeSO_3]$ was measured at temperatures of (322.15, 317.45, 312.45, and 307.55) K and pressures ranging from (4 to 9) MPa. The solubility data are presented in Table 1. The solubility behavior of CO_2 in ILs with temperature and pressure was shown in Figures 2 and 3. It can be found that the solubility of CO_2 in all the studied ILs increases with increasing pressure and decreases with increasing temperature; the difference of the solubility of CO_2 in different ILs is not dramatic on the basis of molality.

From Figures 2 and 3, it can be seen that the solubility of CO_2 in $[P_{6,6,6,14}][MeSO_3]$ is higher than that in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$. For example, at 7.9 MPa and 312.45 K, the solubility of CO_2 is 4.517 mol·kg^{-1} in $[P_{6,6,6,14}][MeSO_3]$ compared to 3.578 mol·kg^{-1} in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$.

The Henry's law constants at different temperatures are shown in Table 2. From Table 2, it can be seen that the Henry's law constant of all the studied systems increases

Table 1. Solubility of CO_2 in Sulfonate Ionic Liquids

322.15 K		317.45 K		312.45 K		307.55 K	
$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$	$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$	$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$	$\frac{P}{\text{MPa}}$	$\frac{m_{CO_2}}{\text{mol·kg}^{-1}}$
			$[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$				
8.96	3.92	8.63	4.03	8.28	3.95	7.92	4.25
8.58	3.45	8.28	3.56	7.9	3.58	7.62	3.68
8.13	3.10	7.79	3.23	7.48	3.28	7.14	3.39
7.8	2.88	7.48	3.00	7.16	3.13	6.86	3.19
7.04	2.61	6.74	2.71	6.47	2.80	6.19	2.89
6.09	2.23	5.85	2.30	5.62	2.39	5.38	2.47
5.22	1.91	5.04	1.97	4.84	2.06	4.63	2.17
			$[P_{6,6,6,14}][MeSO_3]$				
8.73	4.15	8.32	4.25	7.91	4.52	7.48	4.87
8.44	3.60	8.03	3.84	7.64	3.98	7.23	4.27
7.64	3.24	7.28	3.41	6.93	3.61	6.57	3.75
6.96	3.00	6.66	3.10	6.35	3.33	6.03	3.39
6.38	2.70	6.09	2.82	5.81	2.96	5.53	3.06
5.72	2.39	5.47	2.48	5.22	2.63	4.97	2.72
5.12	2.17	4.94	2.23	4.74	2.36	4.48	2.48

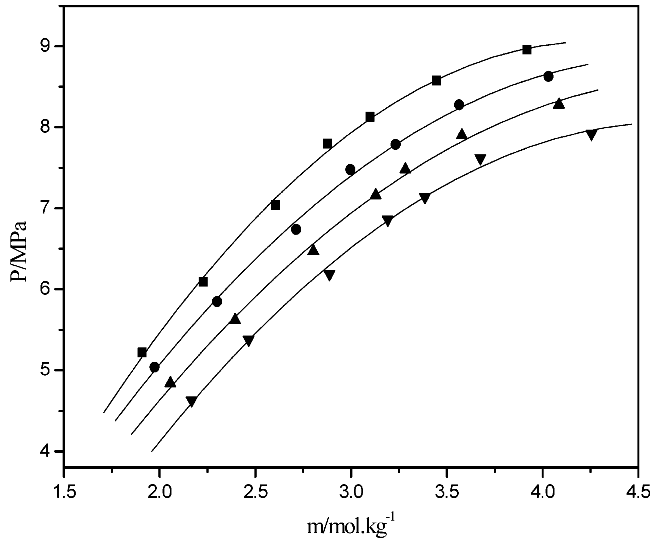

Figure 2. CO_2 solubility in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$: ■, 322.15 K; ●, 317.45 K; ▲, 312.45 K; ▼, 307.55 K; —, correlation of experimental work.

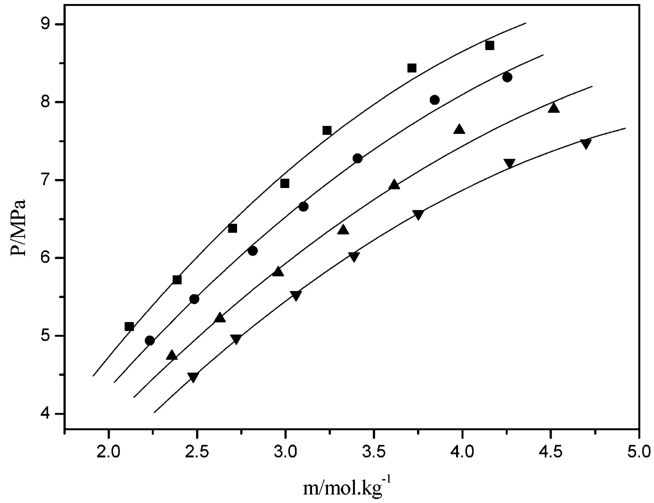

Figure 3. CO_2 solubility in $[P_{6,6,6,14}][MeSO_3]$: ■, 322.15 K; ●, 317.45 K; ▲, 312.45 K; ▼, 307.55 K; —, correlation of experimental work.

with increasing temperature, which indicates the solubility of CO_2 decreases with increasing temperature. At a given temperature, the magnitude of the Henry's law constants

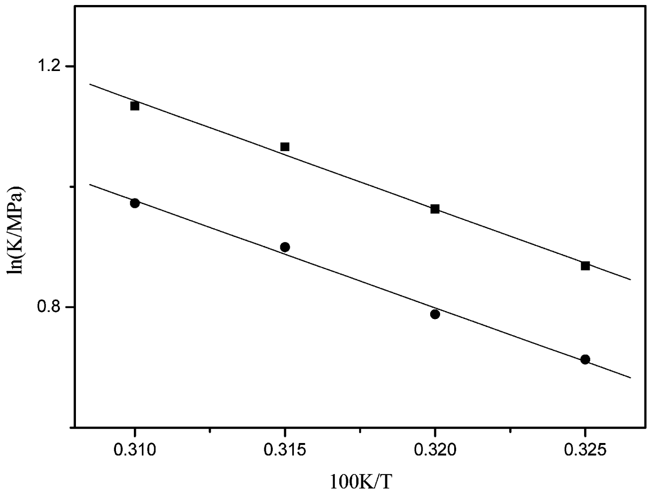

Figure 4. Effect of temperature on the Henry's law constant for CO_2 in ILs: ■, $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$; ●, $[P_{6,6,6,14}][MeSO_3]$; —, correlation of experimental work.

Table 2. Henry's Law Constant of CO_2 in Sulfonate Ionic Liquids

$\frac{T}{\text{K}}$	$\frac{K_H}{\text{MPa}}$	SD[a]
	$[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$	
322.15	3.11	0.077
317.45	2.90	0.057
312.45	2.62	0.048
307.55	2.38	0.060
	$[P_{6,6,6,14}][MeSO_3]$	
322.15	2.65	0.043
317.45	2.46	0.044
312.45	2.20	0.034
307.55	2.04	0.029

[a] Standard deviation.

of CO_2 dissolved in ILs follows the sequence $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3] > [P_{6,6,6,14}][MeSO_3]$.

The logarithms of the Henry's law constant variation versus the inverse of temperature are shown in Figure 4, from which the standard enthalpy, standard Gibbs free energy, and standard entropy are calculated, and the results are presented in Table 3. The negative enthalpy values show that CO_2 exhibits stronger molecular interactions with ILs than with some organic molecules, for example, -20.4 kJ·mol^{-1} in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$ and

Table 3. Standard Enthalpy, Gibbs Free Energy, and Entropy of Solution of CO_2 in Sulfonate Ionic Liquids

	$\Delta_{sol}H°$	$\Delta_{sol}G°$	$\Delta_{sol}S°$
ionic liquid	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
$[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$	−20.4	1.57	−73.6
$[P_{6,6,6,14}][MeSO_3]$	−12.6	1.35	−46.7

−12.6 kJ·mol^{-1} in $[P_{6,6,6,14}][MeSO_3]$ compared to −9.667 kJ·mol^{-1} in heptane, −5.556 kJ·mol^{-1} in cyclohexane, and −9.337 kJ·mol^{-1} in benzene,[21] which means that the CO_2 dissolving in ILs is more favorable enthalpically. However, the negative entropy values indicate a higher ordering degree when CO_2 is dissolved in ILs, which means the CO_2 dissolving in ILs is not favorable. As a result, the standard Gibbs free energy shows small positive values.

Conclusion

The solubility of CO_2 in the sulfonate ILs $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$ and $[P_{6,6,6,14}][MeSO_3]$ was determined at temperatures of (322.15, 317.45, 312.45, and 307.55) K and pressures ranging from (4 to 9) MPa. The results show that the difference of the solubility of CO_2 in two kinds of sulfonate ILs is not dramatic on the basis of molality. The solubility of CO_2 in $[P_{6,6,6,14}][MeSO_3]$ is higher than that in $[P_{6,6,6,14}][C_{12}H_{25}PhSO_3]$. The experimental data were correlated by means of the extended Henry's law. It shows that the Henry's law constant of CO_2 in all the studied ILs increases with increasing temperature. The standard enthalpy, standard Gibbs free energy, and standard entropy were obtained. The standard Gibbs free energy shows a small positive value.

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