Solubility of CO_2 in Propanone, 1-Ethyl-3-methylimidazolium Tetrafluoroborate, and Their Mixtures[†]

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Solubility data of carbon dioxide (CO_2) (1) in propanone (2), 1-ethyl-3-methylimidazolium ($[EMIM]^+[BF4]^-$) (3), and their mixtures ($w_3 = 0.10$, 0.20, and 0.50) at temperatures (298.2 and 313.2) K and pressures up to 8.0 MPa were measured by means of a high-pressure view-cell technique. Henry's law was applied to correlate the experimental data, and it was found that the magnitude of Henry's constants for propanone ($w_3 = 0.0$), $[EMIM]^+[BF4]^-$ ($w_3 = 1.0$), and their mixtures follows the order of $w_3 = 0.0 < w_3 = 0.10 < w_3 = 0.20 < w_3 = 0.50 < w_3 = 1.0$ at a given temperature. The mixtures of propanone and $[EMIM]^+[BF4]^-$ may be used as promising solvents for capturing CO_2 since they combine the advantages of organic solvents and ionic liquids.

Introduction

In recent years, ionic liquids (ILs) have received significant attention because they offer many excellent properties,[1−3] such as (1) high chemical stability, (2) less caustic, (3) good solvents for polar and nonpolar compounds, (4) nonvolatility, and (5) good performance in separation and reaction processes. For capturing CO_2 to reduce greenhouse gas emissions, a great number of experimental data on the solubility of CO_2 in ILs at high pressures and above room temperature have been reported,[4−14] which are important design parameters in establishing equilibrium stage (EQ) and nonequilibrium stage (NEQ) mathematical models to simulate and optimize the absorption and stripping columns. However, compared with traditional organic solvents, the high viscosity and cost of ILs may become some obstacles for their application in industry.

As we know, propanone as a polar but nonassociated solvent is used for absorbing CO_2 in industry. Many researchers have reported the vapor−liquid equilibrium (VLE) data for CO_2 + propanone,[15−18] and the results showed that the solubility of CO_2 in propanone is greater than other physical solvents, such as methanol,[19−24] ethanol,[15,16,21,23] and so on.[17−20,23−30] However, its high volatile quality makes the separation process and solvent recycling usage hardly viable, which demands high energy. ILs might serve as a superior additive which can counteract this disadvantage brought out by traditional physical solvents. The mixtures of propanone and ILs as absorbing agents for capturing CO_2 combine the advantages of organic solvents and ILs and reduce propanone's volatility. Moreover, they may substitute the current propanone process only by replacing the separating agent without changing the whole flowsheet. However, only very few investigations[31−34] on gas−liquid equilibrium for CO_2 (1) + propanone (2) containing ionic liquids (3) have been done currently, and no systematic solubility data are reported.

The IL, i.e., 1-ethyl-3-methylimidazolium ($[EMIM]^+[BF4]^-$), was selected in this study because it was much easier to obtain from chemical markets at a lower price. Moreover, there are a very limited number of VLE data reported[8] for the system of CO_2 (1) + $[EMIM]^+[BF4]^-$ (2) only at temperature 298.15 K and pressures from (0.251 to 0.875) MPa so that we can not compare the solubility of CO_2 in $[EMIM]^+[BF4]^-$ with those in various ILs including a bis(trifluoromethylsulfonyl)imide (Tf_2N) anion which can be found from the ILs database (see http://ilthermo.boulder.nist.gov/ILThermo). Therefore, the solubility data of CO_2 on the binary and ternary systems of CO_2 (1) + propanone (2), CO_2 (1) + $[EMIM]^+[BF4]^-$ (2), and CO_2 (1) + propanone (2) + $[EMIM]^+[BF4]^-$ (3) were measured at temperatures (298.2 and 313.2) K and pressures up to 8.0 MPa, which will be the essential data for capturing CO_2 efficiently and effectively.

Experimental Section

Chemicals. The ionic liquid $[EMIM]^+[BF4]^-$ was provided by the Chemical Engineering Institute of the Normal University of Hebei (China), with a mass fraction purity > 98 % observed by liquid chromatography and no Cl^- anion detected (the detection limit 0.1 $g \cdot L^{-1}$). Furthermore, before the experiments, the IL was dried for 48 h at (348 to 358) K under a vacuum by the rotary evaporator to separate the IL from volatile byproducts and water. After experiments, the IL was reused after the rotary evaporation to eliminate the volatile components, and no color change of IL was found. The water mass fraction in IL determined by Karl Fisher titration was less than 0.002. Propanone was purchased from Beijing modern eastern fine chemicals with a mass fraction purity of > 0.995. CO_2 was purchased from Longkou City Gas Plant, with a mass fraction purity > 0.9999. Sodium sulfate (Na_2SO_4) with a mass fraction purity > 0.990 and sulfuric acid (H_2SO_4) with a mass fraction purity of between (0.95 and 0.98) % were purchased from Beijing Chemical Plant.

Apparatus and Procedure. The solubility data were measured by means of a high-pressure view-cell technique, which is showed schematically in Figure 1. The apparatus mainly consisted of a CO_2 cylinder, a computer-controlled metering syringe pump (made by Beijing Satellite Manufacturing Fac-

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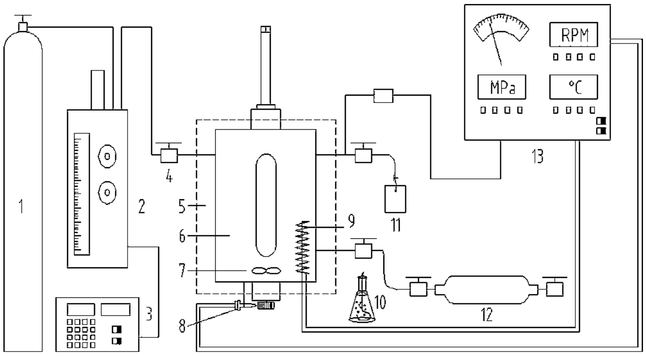

Figure 1. Experimental apparatus for solubility measurement: 1, CO_2 cylinder; 2, syringe pump; 3, pressure and flow rate display; 4, pressure transducer; 5, thermostat cover; 6, high-pressure view cell; 7, magnetic stirrer; 8, electric motor; 9, thermocouple; 10, sodium sulfate solution; 11, airbag; 12, sampler; 13, pressure and temperature display.

tory), a volume-variable high-pressure stainless steel view cell, a magnetic stirrer, and two samplers taking out gas and liquid samples, respectively. The temperature was monitored with a thermocouple and a digital thermometer with an uncertainty of 0.1 K. The pressure gauge consisted of a pressure transducer and an indicator calibrated by a high-precision pressure gauge before experiments with an uncertainty of 0.01 MPa in the pressure range of (0 to 20) MPa.

A certain amount of solvent (about 35 mL) was first loaded into the cell. Then air was purged from the system with CO_2 several times. The cell was controlled at a predetermined temperature. As CO_2 entered the cell by a syringe pump, it was dissolved into the solvent, and the system pressure decreased gradually. It was assumed that gas−liquid equilibrium had been reached until the system pressure was invariable for about 2 h.

A small amount of gas sample was collected with an airbag and was detected by gas chromatography. The gas chromatography (GC 4000A) was equipped with a TCD detector. The chromatographic column (3 m × 0.3 mm) was packed with Porapak-Q. The carrier gas was hydrogen flowing at 30 $cm^3 \cdot min^{-1}$, and the operating conditions were as follows: the injector, oven, and detector temperatures at 353.2 K. The maximum uncertainty of gas mole fractions was 0.003. The liquid sample (about (1.5 to 2.0) g) was collected in the sample bomb, from which CO_2 was released slowly and then absorbed into the aqueous solution of Na_2SO_4 with pH (between 2.5 and 3.0) adjusted by H_2SO_4 to trap the volatile organic solvent that is desorbed from CO_2 as well and thus realize a more complete separation of CO_2 and solvent. The amounts of CO_2 and solvent in the liquid sample were determined using the gravimetric method by measuring the mass difference of solutions with and without CO_2. The mass uncertainty using an electronic balance (CPA 1003S, Sartorius) was 0.001 g. Therefore, the estimated uncertainty of solubility measurement in mole fractions was less

Table 1. Solubility of CO_2 (1) in Propanone (2) + $[EMIM]^+[BF4]^-$ (3) at Different Temperatures and Pressures

	$T = 298.2$ K			$T = 313.2$ K		
	P/MPa	x_1	y_1	P/MPa	x_1	y_1
propanone	0.55	0.1099	0.9514	1.01	0.1490	0.9708
	1.03	0.2033	0.9590	1.52	0.2212	0.9724
	1.53	0.2989	0.9622	2.00	0.2927	0.9759
	2.05	0.3960	0.9799	2.43	0.3500	0.9759
	2.50	0.4665	0.9747	3.00	0.4322	0.9845
	3.02	0.55607	0.9682	3.54	0.5075	0.9861
	3.54	0.6311	0.9826	4.00	0.5654	0.9856
	4.04	0.7193	0.9845	4.60	0.6474	0.9866
	4.60	0.8054	0.9869	5.01	0.7001	0.9642
	5.16	0.8847	0.9520	5.51	0.7587	0.9508
	5.51	0.9339	0.9541	6.03	0.8234	0.9504
				7.02	0.9326	0.9560
$w_3 = 0.1$ IL + $w_2 = 0.9$ propanone	0.52	0.0955	0.9380	0.52	0.0689	0.9242
	1.01	0.1855	0.9688	1.00	0.1337	0.9485
	1.49	0.2724	0.9773	1.50	0.2060	0.9727
	2.03	0.3670	0.9836	2.05	0.2843	0.9735
	2.51	0.4421	0.9854	2.50	0.3431	0.9737
	3.06	0.5341	0.9875	3.07	0.4228	0.9781
	3.54	0.6200	0.9882	3.57	0.4862	0.9795
$w_3 = 0.2$ IL + $w_2 = 0.8$ propanone	0.53	0.0887	0.9468	0.54	0.0608	0.8853
	1.00	0.1758	0.9667	1.00	0.1168	0.9270
	1.50	0.2646	0.9771	1.55	0.1839	0.9487
	2.01	0.3590	0.9819	2.04	0.2491	0.9692
	2.50	0.4278	0.9856	2.52	0.3097	0.9734
				3.03	0.3813	0.9829
$w_3 = 0.5$ IL + $w_2 = 0.5$ propanone	0.60	0.0792	0.9510	0.54	0.0526	0.9466
	1.02	0.1349	0.9783	1.02	0.0970	0.9246
	1.55	0.2011	0.9638	1.50	0.1414	0.9234
	2.03	0.2617	0.9843	2.00	0.1981	0.9781
	2.54	0.3208	0.9823	2.50	0.2437	0.9790
				3.00	0.2983	0.9842
$[EMIM]^+[BF_4]^-$	0.53	0.0555	1.0000	0.56	0.0425	1.0000
	0.91	0.0918	1.0000	1.01	0.0763	1.0000
	1.55	0.1470	1.0000	1.50	0.1147	1.0000
	2.01	0.1875	1.0000	1.57	0.1197	1.0000
	2.50	0.2274	1.0000	2.01	0.1510	1.0000
	3.00	0.2700	1.0000	2.52	0.1877	1.0000
	3.50	0.3102	1.0000	3.05	0.2271	1.0000
	4.04	0.3453	1.0000	3.54	0.2576	1.0000
				4.06	0.2891	1.0000

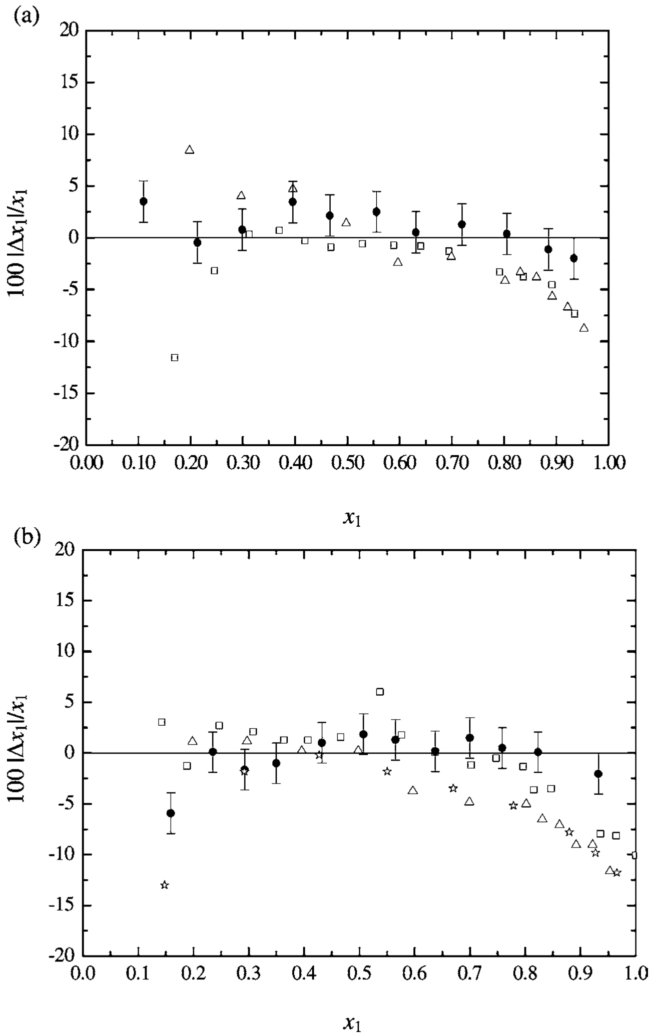

Figure 2. Relative deviations $|\Delta x_1|/x_1 = |x(\text{exptl}) - x(\text{calcd})|/x(\text{exptl})$ between the calculated and measured solubility in mole fractions of CO_2 in propanone at 298.2 (a) and 313.2 K (b): ●, this work with error bars representing the extended uncertainty; □, ref 15; △, ref 16; ☆, ref 17.

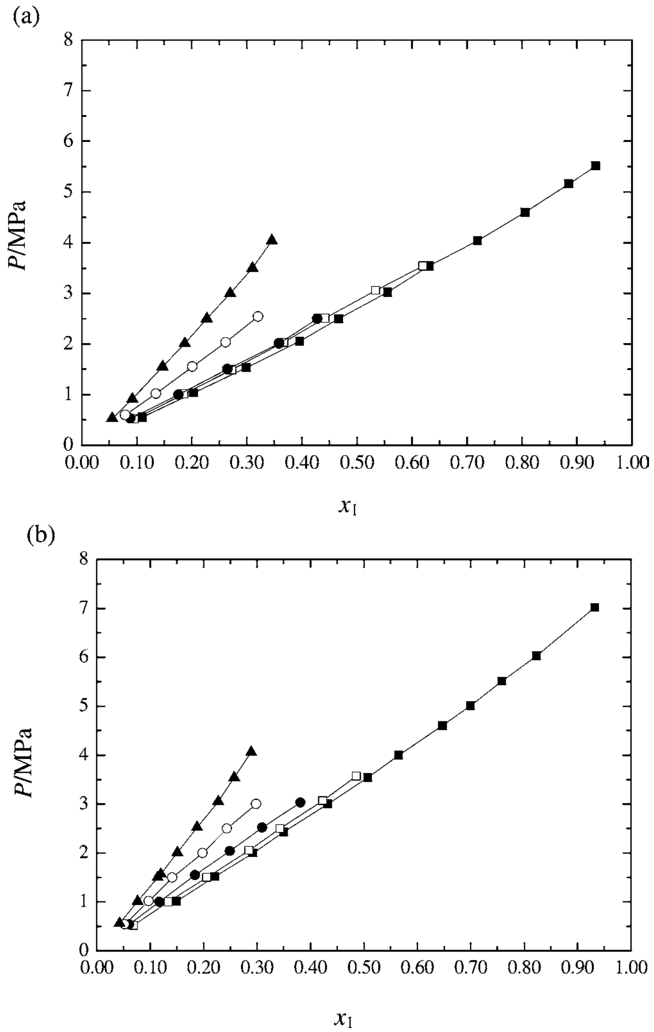

Figure 3. Solubility of CO_2 (1) in the mixtures of propanone (2) + $[EMIM]^+[BF_4]^-$ (3) at 298.2 K (a) and 313.2 K (b): ■, propanone; □, 10 wt % IL + 90 wt % propanone; ●, 20 wt % IL + 80 wt % propanone; ○, 50 wt % IL + 50 wt % propanone; ▲, IL.

than 0.00002. For each data point, three runs were performed to check the reproducibility of the results at the same temperature and pressure, which also indicates that no degradation of IL was produced.

Results and Discussion

To test the performance of the experimental apparatus, the solubility of CO_2 (1) in propanone (2) was measured at temperatures of (298.2 and 313.2) K and pressures up to 8.0 MPa. The vapor−liquid equilibria for the binary system of CO_2 (1) + propanone (2) are listed in Table 1, where x_1 is the mole fraction of CO_2 in solution and y_1 is the mole fraction of CO_2 in gas. The experimental results were compared to those by Day et al.,[15] Chiu et al.,[16] and Adrian et al.,[17] as shown in Figure 2. Our experimental data were in good agreement with those reported in the literature with the maximum relative deviation between the calculated and measured solubility in mole fractions of CO_2 in the liquid phase of $|\Delta x_1|/x_1$ about 0.10, thus verifying that the experimental apparatus was reliable. Herein, the measured solubility, i.e., x(exptl), represents the experimental data coming from the references and this work, and the calculated solubility data, i.e., x(calcd), were obtained by linear regression using our experimental data at the same temperatures and pressures as the measured solubility because the experimental pressures between our measurement and reference data can not be exactly the same.

In this way, measurements were made for the solubility of CO_2 (1) in the mixtures of propanone (2) and $[EMIM]^+[BF4]^-$ (3) in which the mass fractions of $[EMIM]^+[BF4]^-$ were kept at $w_3 =$ 0, 0.1, 0.2, 0.5, and 1 on a CO_2-free basis. The solubility data at temperatures (298.2 and 313.2) K and pressures up to 8.0 MPa are also listed in Table 1, which comprises the equilibrium mole fractions of CO_2 in liquid and gas phases (x_1, y_1), equilibrium temperature (T), and pressure (P) at different IL contents. It should be mentioned that CO_2 may induce a liquid−liquid phase split for homogeneous mixtures containing IL and polar organic solvent at high pressure, as pointed out by Aki et al.[31] and Mellein and Brennecke.[32] We confirmed this experimental phenomenon, and thus the solubility measurements were carried out below the lower-critical end point pressure (LCEP) which is the locus segmenting the homogeneous liquid phase and two liquid phases.

The P, x diagrams are plotted in Figure 3, and it can be seen that as the pressure increases the CO_2 solubility increases almost linearly, indicating that CO_2 is physically absorbed.[33−38] However, the CO_2 solubility decreases with rising temperature. The solubility trend in the mixtures of propanone and $[EMIM]^+[BF4]^-$ is remarkably similar to that in pure solvents. Moreover, under the same temperature and pressure, CO_2

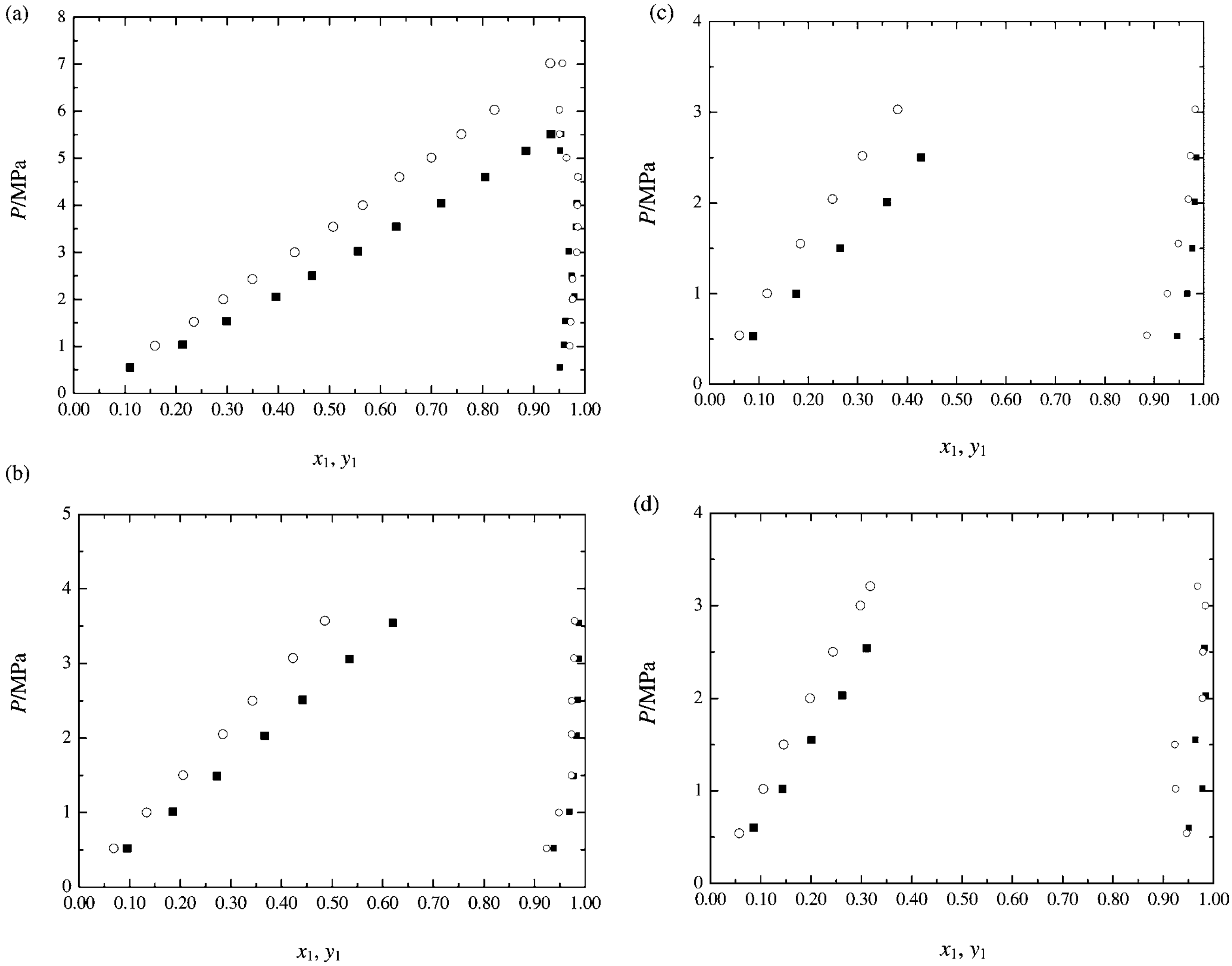

Figure 4. P, x_1, y_1 diagram for CO_2 (1) + propanone (2) + $[EMIM]^+[BF_4]^-$ (3) at $w_3 = 0.0$ (a), 0.10 (b), 0.20 (c), 0.50 (d): ■, 298.2 K; ○, 313.2 K.

exhibits the highest solubility in propanone, while the solubility of CO_2 in $[EMIM]^+[BF4]^-$ is the lowest. The mixtures lie in-between, following the order of $w_3 = 0.0 > w_3 = 0.10 > w_3 = 0.20 > w_3 = 0.50 > w_3 = 1.0$. On the other hand, as shown in Figure 4, as the temperature increases, the amount of propanone in the gas phase also increases. That is to say, the higher the temperature, the more the volatile solvent loss. However, there is no appreciable amount of ILs solubilized into the CO_2 phase. Therefore, the mixtures of propanone and ILs combine the advantages of organic solvents and ILs and can tune the solubility at different IL concentrations.

The Henry's constants[39,40] of CO_2 in propanone, $[EMIM]^+$-$[BF4]^-$, and their mixtures can be defined as

$$H_1(T, P) = \lim_{x_1 \to 0} \frac{f_1^L}{x_1} \tag{1}$$

where f_1^L is the fugacity of CO_2 (1) in the liquid phase. At an equilibrium state, fugacity of CO_2 (1) in the liquid and gas phases is equal.

$$f_1^L(T, P, x_1) = f_1^V(T, P, y_1) = y_1 P \phi_1(T, P, y_1) \tag{2}$$

where y_1 is the mole fraction of CO_2 in the gas phase, and $\phi_1(T, P, y_1)$ is the fugacity coefficient of CO_2 in the gas mixture. Since the mole fraction of CO_2 in the gas phase y_1 is close or equal to unity under the experimental conditions, eq 1 could be rewritten as

$$H_1(T, P) = \lim_{x_1 \to 0} \frac{f_1^L}{x_1} = \lim_{x_1 \to 0} \frac{y_1 P \varphi_1(T, P)}{x_1} \tag{3}$$

where $\phi_1(T, P)$ is the fugacity coefficient of pure CO_2 and is calculated from the equation of state by Span and Wagner.[41]

Henry's constants were estimated by linear extrapolation at $x_1 \to 0$ from the ratio of fugacity to mole fraction of CO_2, f_1/x_1, and the estimated results are given in Table 2. It was found that Henry's constants increase with increasing temperature but at a given temperature follow the order of $w_3 = 0.0 < w_3 = 0.10 < w_3 =$

Table 2. Henry's Constant of CO_2 in Propanone, $[EMIM]^+[BF4]^-$, and Their Mixtures at Zero Pressure (On the Mole Fraction Scale)

	$H_1(T, P)$	
	$T = 298.2$ K	$T = 313.2$ K
propanone	4.79	6.61
$w_3 = 0.1$ IL + $w_2 = 0.9$ propanone	5.11	7.01
$w_3 = 0.2$ IL + $w_2 = 0.8$ propanone	5.58	7.92
$w_3 = 0.5$ IL + $w_2 = 0.5$ propanone	7.06	9.68
$[EMIM]^+[BF_4]^-$	9.74	13.02

$0.20 < w_3 = 0.50 < w_3 = 1.0$, which is contrary to the trend of solubility data.

Conclusions

Experimental results are present for the solubility data of CO_2 (1) in propanone (2), 1-ethyl-3-methylimidazolium ($[EMIM]^+$-$[BF4]^-$), (3) and their mixtures ($w_3 = 0.10$, 0.20, and 0.50) at temperatures (298.2 and 313.2) K and pressures up to 8.0 MPa. The Henry's constants were obtained by extrapolation procedure, following the order of $w_3 = 0.0 < w_3 = 0.10 < w_3 = 0.20 < w_3 = 0.50 < w_3 = 1.0$ at a given temperature. The mixtures of propanone and IL may be promising absorbing agents for capturing CO_2 due to the combination of advantages of organic solvents and ILs. The new data help to evaluate the separation ability of different solvents such as organic solvents, ILs, and their mixtures and to design the feasible process for capturing CO_2 efficiently and effectively. Furthermore, the solubility data can also be used for some synthetic chemistry in which ILs are required to recover from volatile organic solvents utilizing CO_2 and for stimulant detections in which volatile drugs are extracted by the double actions of CO_2 and IL.

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