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Physical Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate/*N*-Methyl-2-pyrrolidone Mixtures and the Solubility of CO_2 in the System at Elevated Pressures

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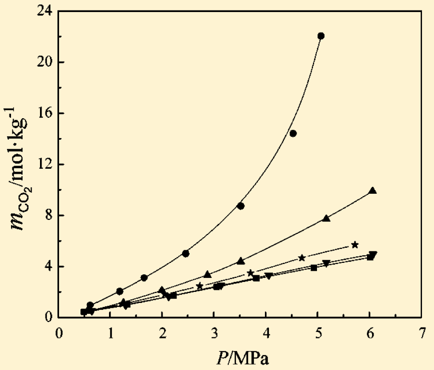
ABSTRACT: Densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) (1) + *N*-methyl-2-pyrrolidone (NMP) (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 at T = (298.15 to 318.15) K were measured and fitted to standard equations. The results show that densities and viscosities of the hybrid solvents decrease with the increase of temperature and mass fraction of NMP. A high-pressure variable-volume view cell technique was used to determine the solubility of CO_2 in pure solvents and mixtures under elevated pressures up to 6 MPa at temperatures from (298.15 to 318.15) K. The results indicate that the solubility of CO_2 in the pure solvents and mixtures increases with the increase of pressure and with the decrease of temperature. The solubility of CO_2 in the mixtures increases with the increase of the mass fraction of NMP, but it is very close to that in pure [bmim][BF_4] as the mass fraction of NMP is around 0.1019.



■ INTRODUCTION

Carbon dioxide (CO_2) is one of the greenhouse gases which may lead to the global-warming, and the emissions of CO_2 from burning of fossil fuels have caused great concern all over the world. Currently, there are many technologies developed for the removal of CO_2.[1−3] One of the technologies is to employ aqueous amines, such as methyldiethanolamine, monoethanolamine, and diethanolamine, as chemical solvents to absorb CO_2. They are used commercially for a high CO_2 absorption capacity. However, there are several drawbacks of this technology, such as corrosion problems, high volatility of amines, and high energy consumption for desorption.[4] Using physical solvents such as methanol, *N*-methyl-2-pyrrolidone (NMP), propylene carbonate (PC), and dimethylether of poly(ethylene glycol) is also an efficient way to capture CO_2. Methanol is one of the most studied and used solvents, and it shows great advantages when used at higher CO_2 pressures. However, methanol needs extremely low operating temperatures for its high vapor pressure.[2] Therefore, nonvolatile liquid solvents with a high capacity may be more attractive for the removal of CO_2. Currently, ionic liquids (ILs) have drawn much attention for their negligible vapor pressure, low toxicity, high thermal stability, and tunable structure.

Many groups have studied the solubility of CO_2 in different kinds of ILs. Blanchard et al.[5] found that ILs can dissolve massive amounts of CO_2, while the solubility of ILs in supercritical CO_2 was extremely low. Since then, the absorption of CO_2 with ILs has drawn much attention all over the world. The ILs used to absorb CO_2 can be classified into normal ILs and task-specific ILs. CO_2 can be only physically soluble in the normal ILs, and its solubility increases with increasing pressure and decreasing temperature.[6−13] Bates et al.[14] reported the first task-specific IL used to absorb CO_2 at ambient pressure and room temperature; the uptake of CO_2 per mole IL could reach to 0.5 which was very close to the theoretical maximum capacity of the IL. After that, many kinds of task-specific ILs were reported.[11,15−21] The studies of the absorption of CO_2 by ILs have made great progress, and ILs have a potential use in real industries. However, the viscosities of pure ILs are often much higher than those of traditional organic solvents. These disadvantages of ILs severely limit their applications. Many researchers have reported the viscosities of ILs with water or organic solvents and found that the viscosities of pure ILs decrease sharply by adding small amounts of molecular solvents.[22−26] As a result, the blends of ILs with other solvents may show great advantages when used for the removal of CO_2.[27,28] Actually, the absorption of CO_2 by the hybrid solvents has been widely studied.[4,29−35]

As is known, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) is one of the most efficient ILs for its high absorption capacity of CO_2,[36] and NMP is the solvent used in the Purisol process[37] for its wonderful properties, such as low vapor pressure, low viscosity, and high CO_2 absorption capacity. In this work, we selected NMP as a cosolvent to improve the high viscosity of [bmim][BF_4], and we studied the physical properties such as densities and viscosities of [bmim][BF_4] (1) + NMP (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 at T = (298.15 to 318.15) K. Besides, the solubilities of CO_2 in pure solvents and the hybrid solvents were determined at 298.15 K under elevated pressures,

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and the influence of temperature on solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with w_1 = 0.6999 was also investigated.

■ EXPERIMENTAL SECTION

Chemicals. CO_2 with a 0.99995 mole fraction purity was supplied by Beijing Haipu Gases Co. (Beijing, China). [Bmim][BF_4] with a 0.99 mass fraction purity was purchased from Henan Lihua Pharmaceutical Co., Ltd. (Henan, China). Before use, the IL was dried under vacuum for more than 12 h at 343.15 K, and the water content in the IL was determined by a Karl Fischer titrator (ZDJ-400S, Beijing Xianqu Weifeng Technology Development Co.) and was found to be not more than 0.0034 mass fraction. The analytical reagent NMP with a purity of more than 0.99 mass fraction was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) and was used as received.

Apparatus and Procedures. Five samples of [bmim]-[BF_4] (1) + NMP (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 were prepared in this work. All of the mixtures were prepared with an analytical balance (BS 224S, Sartorius) with a precision of 0.1 mg. The uncertainty in the mass fraction of all mixtures was estimated to less than ± 0.005. After being well mixed, the samples were stored in a desiccator to avoid any effects of atmospheric humidity.

Density Determination. The densities of the samples were determined using a pycnometer with a volume of 5 cm^3, which was calibrated by distilled water at different temperatures before the experiment. The pycnometer filled with deionized water was kept in a constant temperature water bath for more than 15 min to reach thermal equilibrium. The weight of water in the pycnometer was calculated by the weight difference. According to the mass and density (obtained from the NIST Chemistry Webbook) of pure water, the volume of the pycnometer can be calculated. Densities of the samples were measured from (298.15 to 318.15) K at intervals of 5 K. All of the measurements were carried out in a constant temperature water bath, the temperature of which was maintained within ± 0.1 K by using a temperature controller (model A2, Beijing Changliu Scientific Instrument Co.). The temperature was also monitored by a precision mercury thermometer that had a maximum uncertainty of ± 0.05 K. The calibration of the pycnometer and the measurements of the density were performed at least three times to improve the measuring accuracy. The uncertainty in the volume of the pycnometer was less than 0.001 cm^3, and the uncertainty in the density was estimated to be ± 0.0010 $g\cdot cm^{-3}$.

Viscosity Determination. Viscosities of the samples were determined by a series of gravitational capillary viscometers calibrated with standard oils at temperatures from (298.15 to 318.15) K in the same water bath as mentioned above. In this experiment, we measured the flow time of a given volume of liquid by a digital stopwatch with a precision of 0.01 s. The absolute viscosity (η) was calculated from the following equations.

$$\nu = Ct \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where ν is the kinetic viscosity, C is the viscometer constant ((0.004811, 0.01284, 0.02380, 0.1051, and 0.2875) $mm^2\cdot s^{-2}$ for inner diameters of (0.40, 0.60, 0.80, 1.00, and 1.50) mm, respectively), t is the running time of the liquid, and ρ is the density of the liquid. The reproducibility of the viscosity measurement was better than 1 %.

CO_2 Solubility Determination. The solubilities of CO_2 in pure solvents and mixtures were determined on a high-pressure variable-volume view cell reported in our previous work;[38−40] the schematic diagram of the apparatus is shown in Figure 1, which mainly consisted of a constant temperature water bath, a high-pressure variable-volume view cell, a pressure gauge, a temperature controller, a CO_2 bomb, a sampling tube, a glass tube, a vacuum pump, and a magnetic stirrer. The uncertainty of the temperatures was ± 0.05 K as mentioned above. The pressure gauge was calibrated with a Heise Standard pressure gauge, and the uncertainty was ± 0.025 MPa between (0 and 20) MPa.

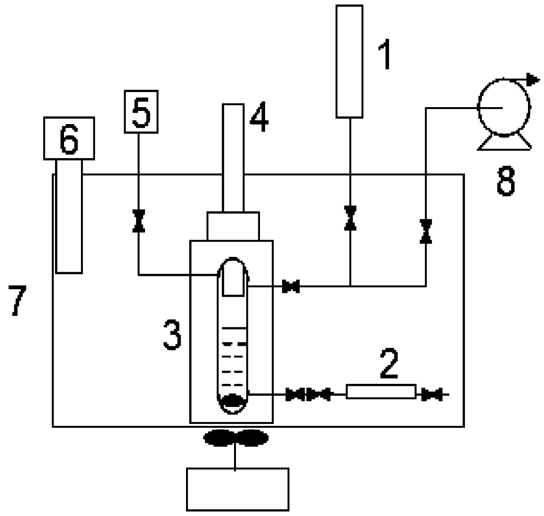

Figure 1. Schematic diagram of the apparatus for the measurement of CO_2 solubility: 1, CO_2 bomb; 2, sampling tube; 3, high-pressure variable-volume view cell; 4, piston; 5, pressure gauge; 6, temperature controller; 7, constant temperature water bath; 8, vacuum pump.

A typical experimental process is described as follows: First, an amount of liquid absorbent (about 30 g) was charged into the view cell, and then the view cell was sealed. Second, the liquid was degassed by a vacuum pump to remove any dissolved gas for at least 0.5 h, and then CO_2 was charged into the view cell through the CO_2 bomb. Third, the view cell was immerged into the water bath, and the magnetic stirrer was started. It should be mentioned that the process of CO_2 dissolution was pretty slow, so we kept the view cell in the water bath for at least 24 h, and we assume that the equilibrium was achieved if the pressure did not change in 3 h. After thermal equilibration, the liquid phase was collected by a sampling tube for analyzing the composition. During the process of sampling, the piston in the view cell was moved to keep the pressure constant, with a fluctuation not more than 0.01 MPa.

The solubility of CO_2 was determined by a gravimetric method. The sampling tube (about 500 g in weight) was used to collect the liquid phase (about 2 g) from the view cell. After sampling, the liquid were dropped into a glass tube (about 35 g). Then, the liquid in the glass tube was degassed by a vacuum pump until the mass of the liquid keep constant. There was a very small quantity of liquid left in the sampling tube, and the residue was also taken into account. The mass of the liquid was calculated by the amount of liquid both in the sampling tube and the glass tube. The total amount of CO_2 and liquid can be calculated by the mass differences of sampling tube before and after sampling. Therefore, the mass of CO_2 can be calculated by subtracting the liquid mass from the total amount. The sampling tube was weighed by an electrical balance with an accuracy of 1 mg (CPA 1003S, Sartorius), and the glass tube was weighed by an electrical balance with an accuracy of 0.1 mg (BS 224S, Sartorius). The experiments were repeated several times to ensure the precision of measurement. The solubility of CO_2 in pure solvents and the mixtures can be calculated as follows:

$$m_T = M_1 - M_0$$

$$m_L = (M_2 - M_0) + (m_1 - m_0)$$

$$n_{CO_2} = \frac{m_T - m_L}{M_{CO_2}} = \frac{(M_1 - M_2) + (m_0 - m_1)}{M_{CO_2}}$$

$$m_{CO_2} = \frac{1000 \cdot n_{CO_2}}{m_L} = \frac{1000}{M_{CO_2}} \cdot \frac{(M_1 - M_2) + (m_0 - m_1)}{(M_2 - M_0) + (m_1 - m_0)} \tag{3}$$

where M_0 is the mass of sampling tube before sampling, M_1 is the mass of sampling tube after sampling, M_2 is the mass of the sampling tube after desorption, m_0 is the mass of the glass tube, m_1 is the mass of the glass tube after desorption, m_T is the total mass of liquid absorbent and CO_2, m_L is the mass of the liquid absorbent, n_{CO_2} is the mole amount of CO_2, and m_{CO_2} is the molality of CO_2. The uncertainties in the solubility of CO_2 are estimated according to the method reported in the literature[41] shown as follows.

$$m_{CO_2} = f(M_0, M_1, M_2, m_0, m_1) \tag{4}$$

$$\delta m_{CO_2} = \left[\left(\frac{\partial m_{CO_2}}{\partial M_0} \right)^2 \cdot (\delta M_0)^2 + \left(\frac{\partial m_{CO_2}}{\partial M_1} \right)^2 \cdot (\delta M_1)^2 + \left(\frac{\partial m_{CO_2}}{\partial M_2} \right)^2 \cdot (\delta M_2)^2 + \left(\frac{\partial m_{CO_2}}{\partial m_0} \right)^2 \cdot (\delta m_0)^2 + \left(\frac{\partial m_{CO_2}}{\partial m_1} \right)^2 \cdot (\delta m_1)^2 \right]^{1/2}$$

$\delta M_0 = 0.001$, $\delta M_1 = 0.001$, $\delta M_2 = 0.001$, $\delta m_0 = 0.0001$, $\delta m_1 = 0.0001$.

The estimated uncertainties for each data point are listed in the data tables.

RESULTS AND DISCUSSION

Density and Viscosity. Table 1 shows the comparison of our experimental data with available values reported in the literature.[22−24,42−45] It can be seen that the property values of NMP and the density values of $[bmim][BF_4]$ show good agreement with the literature data. However, the viscosity of $[bmim][BF_4]$ shows a great discrepancy between our experimental data with the data reported by refs 23 and 24. The main reason for the discrepancy may be that the ILs used by different authors have different purities and water content. But the viscosities of $[bmim][BF_4]$ measured in this work are in good agreement with the results reported by refs 22 and 42. Therefore, the experimental data in this work can be acceptable.

Table 1. Comparison of Experimental Data for $[bmim][BF_4]$ and NMP with Literature Data

		$\rho/g\cdot cm^{-3}$		$\eta/mPa\cdot s$	
substance	T/K	exptl	lit.	exptl	lit.
$[bmim][BF_4]$	298.15	1.2006	1.2015[22]	93.814	94.26[22]
			1.20089[23]		110.308[24]
			1.21105[24]		
	303.15	1.1977	1.1984[22]	71.763	74.21[22]
			1.19734[23]		81.40[23]
			1.195698[42]		68.90[42]
	308.15	1.1948	1.1954[22]	56.407	58.18[22]
	313.10	1.1915	1.1922[a,22]	45.602	46.51[a,22]
			1.19027[a,23]		51.79[a,23]
			1.188618[a,42]		44.73[a,42]
	318.15	1.1884	1.1890[22]	37.322	37.79[22]
NMP	298.15	1.0283	1.02794[43]	1.683	1.683[43]
			1.0279[44]		1.687[44]
			1.02872[45]		1.656[45]
	303.15	1.0245	1.02347[43]	1.558	1.554[43]
	308.15	1.0201		1.470	
	313.10	1.0158	1.01455[a,43]	1.337	1.332[a,43]
			1.01519[a,45]		
	318.15	1.0117		1.248	

[a]The values of densities and viscosities were measured at 313.15 K.

Densities and viscosities of $[bmim][BF_4]$ (1) + NMP (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 at T = (298.15 to 318.15) K are listed in Table 2. The variations of densities and viscosities with temperatures are plotted in Figures 2 and 3, respectively. As can be seen from the figures, the densities of $[bmim][BF_4]$ (1) + NMP (2) show good agreement with the work by Wang et al.,[46] and the densities decrease with the increase of the mass fraction of NMP and temperature. The viscosities of the mixtures show the same trends as the change of densities but are much more sensitive to the content of NMP and temperature. The phenomenon is similar to other ILs with molecule solvents. The result shows that NMP may be a perfect solvent to decrease the high viscosity of $[bmim][BF_4]$.

Table 2. Densities (ρ) and Viscosities (η) of $[bmim][BF_4]$ (1) + NMP (2) at T = (298.15 to 318.15) K

	T/K				
w_1	298.15	303.15	308.15	313.10	318.15
			$\rho/g\cdot cm^{-3}$		
0.0000	1.0283	1.0245	1.0201	1.0158	1.0117
0.5000	1.1156	1.1118	1.1079	1.1041	1.1003
0.6999	1.1488	1.1456	1.1420	1.1383	1.1350
0.8981	1.1820	1.1794	1.1762	1.1731	1.1701
1.0000	1.2006	1.1977	1.1948	1.1915	1.1884
			$\eta/mPa\cdot s$		
0.0000	1.683	1.558	1.470	1.337	1.248
0.5000	8.196	7.291	6.382	5.630	5.045
0.6999	19.327	16.027	13.515	11.632	10.072
0.8981	49.460	39.748	32.429	26.927	22.474
1.0000	93.814	71.763	56.407	45.602	37.322

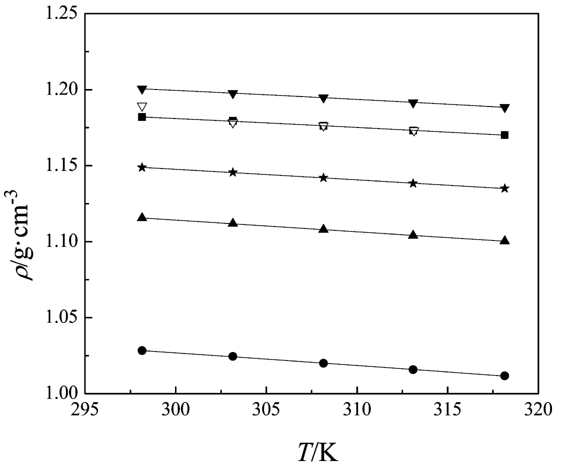

Figure 2. Densities of [bmim][BF_4] (1) + NMP (2) as a function of temperature: ●, $w_1 = 0.0000$; ▲, $w_1 = 0.5000$; ★, $w_1 = 0.6999$; ■, $w_1 = 0.8981$; ▼, $w_1 = 1.0000$; ▽, $w_1 = 0.9010$ (Wang et al.[46]). The solid lines are the results calculated by eq 5.

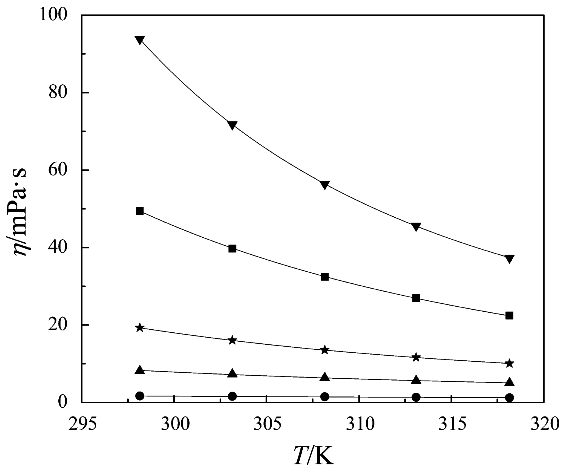

Figure 3. Viscosities of [bmim][BF_4] (1) + NMP (2) as a function of temperature: ●, $w_1 = 0.0000$; ▲, $w_1 = 0.5000$; ★, $w_1 = 0.6999$; ■, $w_1 = 0.8981$; ▼, $w_1 = 1.0000$. The solid lines are the results calculated by eq 6.

Densities and viscosities as a function of temperature were fitted using the following eqs 5 and 6 according to the literature:[42,47,48]

$$\rho/\text{g}\cdot\text{cm}^{-3} = A_0 + A_1(T/\text{K}) + A_2(T/\text{K})^2 \tag{5}$$

$$\eta/\text{mPa}\cdot\text{s} = \exp(B_0 + B_1/(T/\text{K} + B_2)) \tag{6}$$

where T is the temperature, ρ and η are the density and viscosity, respectively, and A_0, A_1, A_2, B_0, B_1, and B_2 are the fitting coefficients. The average absolute deviation (AAD) is defined as follows:

$$\text{AAD} = \frac{1}{n}\sum_{i}^{n}|X_{i,\text{calcd}} - X_{i,\text{exptl}}| \tag{7}$$

where n is the number of experimental points, and X stands for density (ρ) or viscosity (η). The coefficients and standard errors for the densities and viscosities and AAD were presented in Tables 3 and 4, respectively.

Solubility of CO_2 in Pure Solvents and Mixtures. To verify the feasibility of the analysis method in this work, we compared the solubility of CO_2 in [bmim][BF_4] measured in this work with literature,[11,49] and these data were plotted in Figure 4. As can be seen from the figure, our experimental data are in good agreement with the values reported by refs 11 and 49. As a result, the analysis method used in this work is dependable, and the data reported are reliable.

The solubilities of CO_2 in the pure solvents and mixtures at 298.15 K are listed in Table 5 and illustrated in Figure 5. As can be seen from the figure, NMP has a much higher CO_2 absorption capacity than that of [bmim][BF_4]. The solubility of CO_2 in the pure solvents or mixtures increases with the increase of pressure and varies with the increase of NMP mass fraction. We found that the CO_2 absorption capacities in the mixtures were smaller than the sum of that in the two pure solvents with the same mass fraction. For example, the solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with $w_1 = 0.8981$ is almost as the same as that in pure [bmim][BF_4]. It is well-known that the solubility of CO_2 in ILs is mainly influenced by the anions of ILs. When mixed with organic solvents, strong molecular interactions may be formed between the molecules of the solvents and the anions of ILs, and the volume properties of the mixtures are changed as well as also. Some groups have studied the solubility of CO_2 in the IL/organic mixtures, and their research confirmed the influence of the interactions between ILs and organics on the solubility of CO_2. Brennecke and Mellein[50] studied the solubility of CO_2 in [hmim][Tf_2N]/acetonitrile mixtures at 40 °C and found that the solubility of CO_2 was not enhanced in the mixtures. The reason may be that acetonitrile competes for the anions of IL with CO_2. Peters et al.[51−54] studied the phase behavior of [bmim][BF_4] + 1-(4-isobutylphenyl)-ethanol + CO_2, [bmim]-[BF_4] + 4-isobutylacetophenone + CO_2, [bmim][BF_4] + 1-phenylethanol + CO_2, and [bmim][BF_4] + acetophenone + CO_2; they found that the addition of 1-(4-isobutylphenyl)-ethanol will decrease the solubility of CO_2 in the IL for the reason that hydrogen bonds is formed between the −OH and BF_4^-. Besides, the molecular size of the organic solvents also pays an important role in effecting the solubility of CO_2. For example, the solubility of CO_2 in [bmim][BF_4] + 4-isobutylacetophenone is larger than that in [bmim][BF_4] +

Table 3. Fitting Coefficients and Standard Errors (SE) for the Densities of [bmim][BF_4] (1) + NMP (2) at T = (298.15 to 318.15) K

w_1	A_0	SE	10^3 A_1	10^3 SE	10^6 A_2	10^6 SE	100 AAD
0.0000	1.1553	0.2039	−0.0387	1.3240	−1.2982	2.1482	0.011
0.5000	1.3818	0.0419	−1.0109	0.2720	0.3962	0.4413	0.002
0.6999	1.2865	0.1994	−0.2394	1.2948	−0.7453	2.1009	0.011
0.8981	1.1811	0.1796	0.5711	1.1661	−1.9044	1.8920	0.010
1.0000	1.1757	0.1135	0.7361	0.7368	−2.1884	1.1955	0.006

Table 4. Fitting Coefficients and Standard Errors (SE) for the Viscosities of [bmim][BF_4] (1) + NMP (2) at T = (298.15 to 318.15) K

w_1	B_0	SE	B_1	SE	B_2	SE	100 AAD
0.0000	−3.2525	0.1611	882.0363	38.9053	−64.6071	11.1662	0.944
0.5000	−3.0529	0.1001	985.4200	19.7443	−107.2431	4.2936	3.202
0.6999	−0.7541	0.1430	349.8132	30.0304	−204.0036	4.6791	0.785
0.8981	−2.1211	0.1989	800.0254	57.5621	−165.3051	5.4335	1.425
1.0000	−0.3686	0.1005	425.3369	19.6270	−211.5212	2.3733	4.349

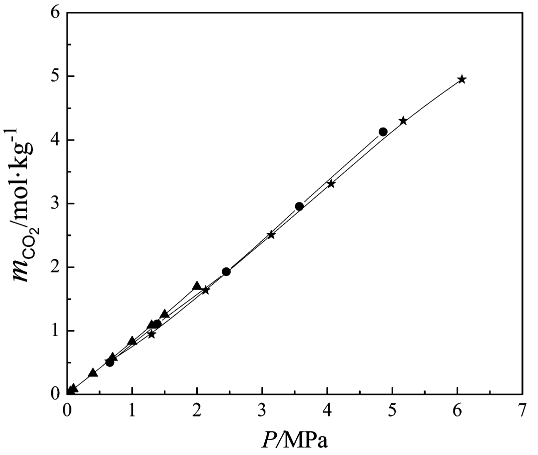

Figure 4. Comparison of the solubility of CO_2 in [bmim][BF_4]: ★, this work (298.15 K); ▲, ref 11 (298 K); ●, ref 49 (298 K).

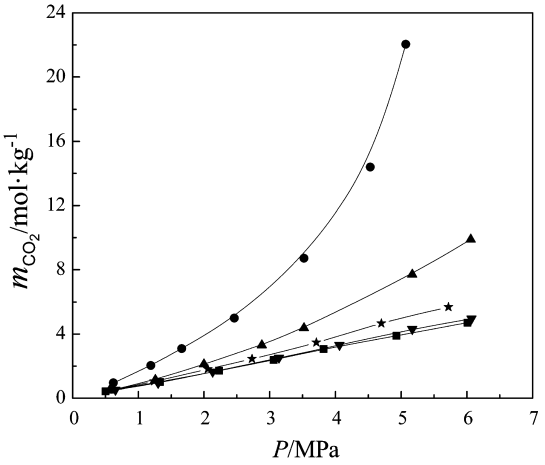

Figure 5. Solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) as a function of pressure at 298.15 K: ●, w_1 = 0.0000; ▲, w_1 = 0.5000; ★, w_1 = 0.6999; ■, w_1 = 0.8981; ▼, w_1 = 1.0000.

acetophenone. The phenomenon can be explained by the fact that the larger molecules may create more free volume in the IL. Lei et al.[35] have studied the solubility of CO_2 in [emim][BF_4], propane, and their mixtures, and the decrease of the solubility of CO_2 in the mixtures was also found. All of these studies suggest that the free volume in the IL/organic mixtures and the interactions between the ILs and the organics can obviously influence the solubility of CO_2. As to the mixtures formed by [bmim][BF_4] and NMP, the decrease of the solubility of CO_2 can be also contributed to the same reason. Wang and Qi[46] studied the densities and volume properties of the binary mixtures formed by [bmim][BF_4] and NMP at T = (298.15 to 313.15) K. The negative excess molar volumes (V^E) for [bmim][BF_4] (1) + NMP (2) indicate a more efficient packing and/or attractive interactions and ion−dipole interactions between the IL and NMP. When mixed, NMP molecules may fit into the interstice of [bmim][BF_4] due to the great difference of molar volumes, which leads to the decrease of the free volume. As a result, the packing effect and the interactions between the ions of [bmim][BF_4] and molecules of NMP may influence the solubility of CO_2 in the mixtures. The volume properties and interactions are different for different compositions of ILs and organic solvents. Therefore, the

Table 5. Solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 at 298.15 K

P	m_{CO_2}	δm_{CO_2}	P	m_{CO_2}	δm_{CO_2}	P	m_{CO_2}	δm_{CO_2}
MPa	mol·kg^{-1}	mol·kg^{-1}	MPa	mol·kg^{-1}	mol·kg^{-1}	MPa	mol·kg^{-1}	mol·kg^{-1}
	w_1 = 0.0000			w_1 = 0.5000			w_1 = 0.6999	
0.62	0.9542	0.0127	0.56	0.4779	0.0181	0.63	0.5325	0.0075
1.19	2.0377	0.0156	1.26	1.1557	0.0137	1.24	1.0508	0.0155
1.66	3.0926	0.0323	2.00	2.1244	0.0138	2.06	1.8158	0.0154
2.46	4.9945	0.0168	2.88	3.3055	0.0150	2.73	2.4547	0.0228
3.52	8.7141	0.0263	3.52	4.3699	0.0529	3.71	3.4735	0.0229
4.53	14.3934	0.0465	5.17	7.7120	0.0352	4.70	4.6638	0.0342
5.07	22.0329	0.0614	6.06	9.8965	0.0260	5.72	5.6770	0.0228
	w_1 = 0.8981			w_1 = 1.0000				
0.50	0.4330	0.0223	0.65	0.5183	0.0088			
1.33	1.0210	0.0103	1.30	0.9443	0.0116			
2.23	1.7103	0.0243	2.13	1.6369	0.0127			
3.06	2.3741	0.0327	3.14	2.5079	0.0169			
3.82	3.0633	0.0284	4.06	3.3085	0.0223			
4.93	3.8846	0.0224	5.17	4.2991	0.0294			
6.01	4.7101	0.0324	6.07	4.9507	0.0164			

Table 6. Solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with w_1 = 0.6999 at T = (298.15, 308.15, and 318.15) K

P	m_{CO_2}	δm_{CO_2}	P	m_{CO_2}	δm_{CO_2}	P	m_{CO_2}	δm_{CO_2}
MPa	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	MPa	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	MPa	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$
	T = 298.15 K			T = 308.15 K			T = 318.15 K	
0.63	0.5325	0.0075	0.66	0.4614	0.0087	0.69	0.4543	0.0159
1.24	1.0508	0.0155	1.35	0.9517	0.0138	1.13	0.6931	0.0185
2.06	1.8158	0.0154	2.18	1.5978	0.0102	2.04	1.2514	0.0169
2.73	2.4547	0.0228	3.03	2.1597	0.0120	3.02	1.8769	0.0105
3.71	3.4735	0.0229	4.13	3.0662	0.0131	3.92	2.5079	0.0130
4.70	4.6638	0.0342	5.05	3.9502	0.0209	5.07	3.2757	0.0261
5.72	5.6770	0.0228	6.04	4.7267	0.0180	5.99	3.9972	0.0256

influence of compositions of the mixtures on the solubility of CO_2 should be further studied.

The temperature is one of the most important factors that should be taken into account for CO_2 absorption. The solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with w_1 = 0.6999 was determined at T = (298.15, 308.15, and 318.15) K, and the results are shown in Table 6 and illustrated in Figure 6.

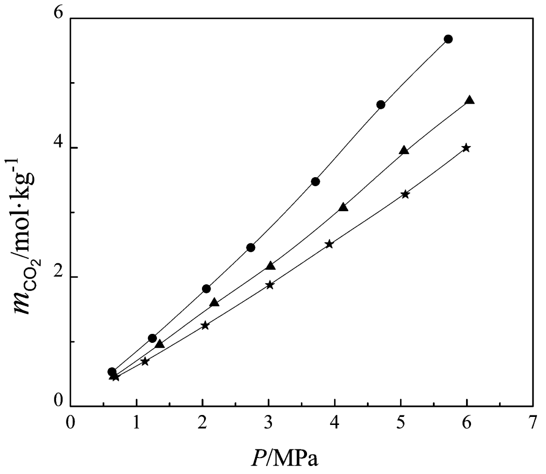

Figure 6. Solubility of CO_2 in [bmim][BF_4] (1) + NMP (2) with w_1 = 0.6999 as a function of pressure at different temperatures: ●, T = 298.15 K; ▲, T = 308.15 K; ★, T = 318.15 K.

It can be seen in Figure 6 that the solubility of CO_2 decreases with the increase of temperature. For example, the solubility of CO_2 at 5 MPa decreases from (3.9502 to 3.2757) $mol \cdot kg^{-1}$ with the temperature increasing from (308.15 to 318.15) K. This phenomenon is similar to the solubility of CO_2 in other solvents. The solubility of CO_2 is sensitive to the change of temperature, so we can regeneration the absorbents by adjusting the temperature.

Henry's constant was calculated by the extended Henry's laws equation:[9,55]

$$k_{H,CO_2}(T) = \lim_{P \to 0}\left[\frac{f_{CO_2}(T,P)}{m_{CO_2}/m^{o}}\right] = \lim_{P \to 0}\left[\frac{y_1 P \phi_{CO_2}(T,P)}{m_{CO_2}/m^{o}}\right] \quad (8)$$

where k_{H,CO_2} (T) is Henry's constant (on the molality scale), ϕ_{CO_2} (T,P) is the fugacity coefficient of pure CO_2 calculated from the Soave–Redlich–Kwong (SRK) equation of state, m_{CO_2} is the molality of CO_2 in pure or mixed solvents, m° = 1 $mol \cdot kg^{-1}$, and y_1 is the mole fraction of CO_2 in the gas phase. Henry's constants are shown in Table 7. We can see that Henry's constant increases with the increase of the mass fraction of the IL at 298.15 K. As to the mixed solvents (w_1 = 0.6999), Henry's constant increases with the increase of temperature.

Table 7. Henry's Constants of CO_2 in Pure or Mixed Solvents (on the Molality Scale)

T/K	w_1	k_H/MPa
298.15	0.0000	0.67
	0.5000	1.16
	0.6999	1.20
	0.8981	1.31
	1.0000	1.36
308.15	0.6999	1.44
318.15	0.6999	1.66

■ CONCLUSIONS

The high viscosity of ILs seriously influences the mass transfer when being applied for the removal of CO_2. Adding another solvent with low viscosity, low vapor pressure, and high CO_2 capacity may be one of the most efficient ways to solve this problem. In this work, we select NMP as the cosolvent for its excellent properties. Densities and viscosities of [bmim][BF_4] (1) + NMP (2) with w_1 = 0.0000, 0.5000, 0.6999, 0.8981, and 1.0000 were measured at T = (298.15 to 318.15) K and fitted to simple equations. The results show that densities of the hybrid solvents decrease with the increase of temperature and mass fraction of NMP. The viscosities also show the same trends as the variations of densities but are more sensitive to the temperature and mass fraction of NMP. The solubilities of CO_2 in the pure solvents and mixtures at elevated pressures up to 6 MPa at temperatures of (298.15, 308.15, and 318.15) K are studied. The results show that the CO_2 solubility in the pure solvents or mixtures increases with the increase of CO_2 pressure and decreases with the increase of temperature. The CO_2 solubility in the mixtures also increases with the mass fraction of NMP, but it is very close to that in pure [bmim][BF_4] as the mass fraction of NMP around 0.1019. Our work suggests that the high viscosity of [bmim][BF_4] can be obviously improved by adding proper amounts of NMP, and the hybrid solvents of [bmim][BF_4] and NMP are excellent absorbents for the removal of CO_2.

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