Solubility of SO_2 in Caprolactam Tetrabutyl Ammonium Bromide Ionic Liquids

Bin Guo, Erhong Duan,* Ailing Ren, Yang Wang, and Haiying Liu

School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang Hebei 050018, People's Republic of China

To explore environmentally benign solvents for absorbing SO_2, a series of caprolactam tetrabutyl ammonium bromide ionic liquids were synthesized, the solubilities of SO_2 in which were measured at (298.2 to 403.2) K and atmospheric pressure. The solubilities of SO_2 in these ionic liquids were 0.680 at 298.2 K and ambient pressure and decreased sharply as temperature increased and increased with the increasing mole ratio of caprolactam. A fifth-order polynomial was proposed and verified by experimental solubility data. The absorption and desorption of SO_2 were practically reversible in the synthesized ionic liquids.

Introduction

SO_2 emission is a significant source of atmospheric pollution when fossil fuels are combusted, causing both environmental and human health concerns due to formation of, e.g., acid rain and smog. For practical use, it is nevertheless difficult to find a material for reversible and selective absorption of SO_2. Water has been found to be a good solvent for SO_2 gas, but when SO_2 gas dissolves in water most of the SO_2 gas reacts with water and converts it into sulfurous acid, which only liberates SO_2 gas on heating. Generally, aqueous liquid amines can be applied for chemically confining SO_2, by formation of ammonium sulfite. However, in the case of large-scale SO_2 capture, amines can evaporate into the gas stream due to their volatility, and the SO_2 proves difficult to desorb from ammonium sulfite.[1−3]

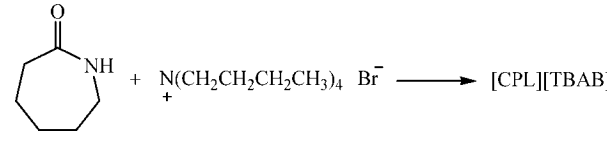
Room-temperature ionic liquids (ILs) are low-melting salts with extremely low vapor pressures, high thermal and chemical stability, and tunable solvent power for many organic and inorganic compounds. Due to these characteristics, they can be used as environmentally benign solvents for a number of applications in the chemical industries.[4,5] The areas of application include gas solubilities and separations, cellulose processing, catalysis, extraction, and high-temperature pyrochemical processing, etc.[6,7] The SO_2 solubility in ILs has gained tremendous interest in recent years. This is because of some major problems that the traditional amine-based solvents experience. ILs can potentially be used as liquid absorbents for permanent gases and as solvents for gas separations without such problems. Thus, Huang et al. prepared 1,1,3,3-tetramethylguanidine (TMG)-based ILs 1,1,3,3-tetramethylguanidine tetrafluoroborate ([TMG][BF_4]) and 1,1,3,3-tetramethylguanidine tetrafluoroborate ([TMG][TF_2N]). The ILs examined were found to absorb a large amount of SO_2 gas corresponding to molar ratios of SO_2 to ILs of 1.33, 1.50, 1.27, and 1.18 (wt %: 20.4, 40.0, 40.1, and 19.2) for 1-butyl-3-methyl imidazolium bis[(trifluoromethyl)sulfonyl]amide ([BMIM][BTA]), 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]), [TMG][BF_4], and 1,1,3,3-tetramethylguanidine bis[(trifluoromethyl)sulfonyl]amide ([TMG][BTA]), respectively, after being saturated with SO_2 gas at 1 bar and 20 °C.[8] They have also found that [BMIM][BF_4] and 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][TF_2N]) can successfully be used for SO_2 gas absorption. However, their separation test for mixed SO_2-N_2 gases was unsuccessful with [BMIM] ILs. Han et al. described a suitable methodology using an IL (TMGL: 1,1,3,3-tetramethylguanidinium lactate) which could absorb 1 mol of SO_2 at 1 bar by formation of the guanidinium sulfurous acid cation. However, a relatively low thermal stability of the IL limited its general practical use, as only part of the absorbed gas could be released upon heating before IL degradation occurred.[9] Zhang et al. synthesized hydroxyl ammonium ionic liquids and found that the solubility of SO_2 in tri(2-hydroxyethyl) ammonium lactate is 0.4957 mol fraction and decreases sharply as temperature increases.[10]

A better understanding of the solubility of SO_2 in ILs is necessary. ILs based on different mole ratios of caprolactam (CPL) and tetrabutyl ammonium bromides (TBAB) were prepared, and the solubilities of SO_2 in them were determined. It is easy and environmentally friendly to synthesize the [CPL][TBAB], and the price of the ILs is very low. The effects of different mole ratios of CPL and TBAB on their capacity for absorption of SO_2 were systematically investigated, and the recovery of SO_2 and recycle of the synthesized ILs were also conducted by increasing temperature and decreasing pressure. In this communication, several ILs were found to be excellent solvents for SO_2 gas.

Experimental Section

Materials. White crystalline caprolactam powder (CAS No. 105-60-2, $C_6H_{11}NO$) was obtained from J&K Chemical Ltd., China, the purity of which was up to 99 %. Tetrabutyl ammonium bromide (CAS No. 1643-19-2, $C_{16}H_{36}NBr$) was bought from Jintan Xinan Chemical Institute, Jiangsu Province, China, the content of which was up to 99.5 %. The ILs of different mole ratio of caprolactam and tetrabutyl ammonium bromide were synthesized following procedures reported else-

Scheme 1. Formation of the Caprolactam Tetrabutyl Ammonium Bromide Ionic Liquids



* To whom correspondence should be addressed. E-mail: deh@tju.edu.cn. Fax: 0086-311-88632009.

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Table 1. Mole Fraction Solubility, x, of SO_2 in [CPL][TBAB] ILs of Different Mole Ratio of Caprolactam and Tetrabutyl Ammonium Bromide

T/K	$10x_i$	RD	T/K	$10x_i$	RD	T/K	$10x_i$	RD	T/K	$10x_i$	RD
					[CPL]/[TBAB] = 1:1						
298.2	6.80	0.001	303.2	6.61	0.005	308.2	6.48	0.002	313.2	6.31	0.002
318.2	6.12	0	323.2	5.96	0.007	328.2	5.67	0.009	333.2	5.52	0
338.2	5.35	0.004	343.2	5.10	0.006	348.2	4.95	0	353.2	4.81	0.006
358.2	4.63	0.002	363.2	4.49	0.004	368.2	4.34	0	373.2	4.20	0.005
378.2	4.08	0.005	383.2	3.97	0.005	388.2	3.90	0.003	393.2	3.78	0.003
398.2	3.67	0.005	403.2	3.51	0.006						
					[CPL]/[TBAB] = 2:1						
298.2	6.54	0.018	303.2	6.11	0	308.2	5.88	0	313.2	5.62	0.011
318.2	5.50	0	323.2	5.38	0.011	333.2	5.05	0.018	338.2	4.70	0.017
343.2	4.54	0.015	348.2	4.44	0	353.2	4.23	0.012	363.2	4.02	0.002
368.2	3.97	0.020	373.2	3.77	0.003	378.2	3.70	0.005	383.2	3.55	0.008
388.2	3.46	0.003	393.2	3.35	0	398.2	3.17	0.009	403.2	3.06	0.10
					[CPL]/[TBAB] = 3:1						
303.2	5.92	0.003	308.2	5.77	0.003	313.2	5.56	0.002	318.2	5.35	0.002
323.2	5.08	0.008	328.2	4.87	0.006	333.2	4.68	0	338.2	4.47	0
343.2	4.30	0.009	353.2	3.92	0.008	358.2	3.71	0.003	363.2	3.54	0.006
368.2	3.40	0.006	373.2	3.30	0.003	383.2	3.06	0.003	388.2	2.92	0.010
393.2	2.86	0	398.2	2.78	0.004	403.2	2.69	0	408.2	2.64	0.011
413.2	2.54	0.004	418.2	2.43	0.008						
					[CPL]/[TBAB] = 4:1						
303.2	5.71	0.004	308.2	5.59	0.005	313.2	5.33	0.002	318.2	5.10	0
323.2	4.82	0.004	328.2	4.57	0.007	333.2	4.37	0	338.2	4.13	0.005
343.2	4.00	0.013	348.2	3.76	0.003	353.2	3.61	0.003	358.2	3.42	0.003
363.2	3.29	0.006	368.2	3.10	0.006	373.2	2.95	0.010	378.2	2.83	0.011
383.2	2.71	0.004	388.2	2.63	0.008	393.2	2.54	0.016	413.2	2.25	0.004
					[CPL]/[TBAB] = 5:1						
308.2	5.51	0.005	313.2	5.33	0.006	318.2	5.14	0.016	323.2	4.75	0.017
328.2	4.57	0.009	333.2	4.36	0.009	338.2	4.35	0.034	343.2	3.87	0.036
348.2	3.77	0.016	353.2	3.67	0.003	358.2	3.64	0.011	363.2	3.27	0.018
368.2	3.28	0.030	373.2	2.89	0.052	378.2	2.84	0.021	383.2	2.84	0.014
388.2	2.60	0.019	393.2	2.50	0.012	398.2	2.42	0	403.2	2.32	0
408.2	2.32	0.043	413.2	2.10	0.014	418.2	2.01	0.020	423.2	1.99	0
					[CPL]/[TBAB] = 6:1						
333.2	4.05	0	338.2	3.89	0.008	343.2	3.82	0.024	348.2	3.40	0.032
353.2	3.33	0.012	358.2	3.08	0	363.2	2.89	0	368.2	2.70	0.004
373.2	2.53	0.008	378.2	2.40	0.004	383.2	2.38	0.038	388.2	2.17	0
393.2	1.94	0.067	398.2	1.98	0	403.2	1.91	0.005	408.2	1.85	0.016
413.2	1.75	0	418.2	1.69	0.006	423.2	1.60	0.006			
					[CPL]/[TBAB] = 7:1						
338.2	3.79	0.003	343.2	3.60	0.008	348.2	3.54	0.028	353.2	3.16	0.013
358.2	2.95	0.007	363.2	2.75	0.011	368.2	2.65	0.011	373.2	2.51	0.008
378.2	2.36	0.004	383.2	2.31	0.026	388.2	2.10	0.019	393.2	2.01	0.010
398.2	1.89	0.016	403.2	1.83	0.005	408.2	1.75	0.011	413.2	1.69	0.018
418.2	1.61	0.012									
					[CPL]/[TBAB] = 9:1						
343.2	3.42	0	348.2	3.38	0	353.2	3.34	0.003	358.2	3.20	0.006
363.2	3.01	0.020	368.2	2.97	0.030	373.2	2.64	0.011	378.2	2.47	0.004
383.2	2.30	0.009	388.2	2.20	0.009	393.2	2.07	0	398.2	2.03	0.020
403.2	1.87	0.016	408.2	1.80	0.006	413.2	1.70	0.006			

where which is expressed in Scheme 1.[11] The [CPL][TBAB] ILs were dried under vacuum at 323.15 K until the mass remained constant. SO_2 with a purity of 99.995 % was supplied by Beijing Analytical Instrument Factory.

Characterization of ILs. ^{1}H NMR spectra were measured on a Bruker AM 400 MHz spectrometer, using DMSO as a solvent with TMS as the internal standard.

Absorption of SO_2 in ILs. The apparatus of absorption of SO_2 in these ILs was prepared following procedures reported elsewhere.[10] A magnetic stirring was used. A precision thermometer was used to determine the adsorption temperature with an uncertainty of ± 0.01 K. The ILs used here were dried and degassed in a vacuum drying oven for at least 24 h at 323.15 K prior to use (10.1 kPa vacuum). SO_2 gas was bubbled with a flow rate of 80 mL·min^{-1} through predetermined amounts of the ILs (about 5 g) loaded in a glass vessel. After 2 h, the mass of the vessel and SO_2 was not changed, and the equilibrium was considered to be reached. The off SO_2 was treated by sodium hydroxide. The gas absorption device did not leak, and the glass vessel was weighed using a balance with an uncertainty of ± 0.0001 g to get the mass of SO_2 absorbed, through which the mole fraction solubilities of SO_2 to ILs can be calculated. The absorption concentration of SO_2 in different mole ratios from 1:1 to 9:1 [CPL][TBAB] ILs versus temperature from (298.2 to 423.2) K was determined at 101.3 kPa.

Recycle of ILs. The absorption and desorption cycles were conducted to study the recovery of SO_2 and recycle of these synthesized ILs. Experiments showed that the solubilities of SO_2 in these synthesized ILs are almost zero at the atmospheric pressure when the temperature rises to 373.2 K at 10.1 kPa vacuum. Consecutive absorption (308.2 K, 101.3 kPa) and desorption (383.2 K, 10.1 kPa vacuum) of SO_2 gas in recycled ILs were studied against times. Standard deviations of the ratios are ± 0.03.

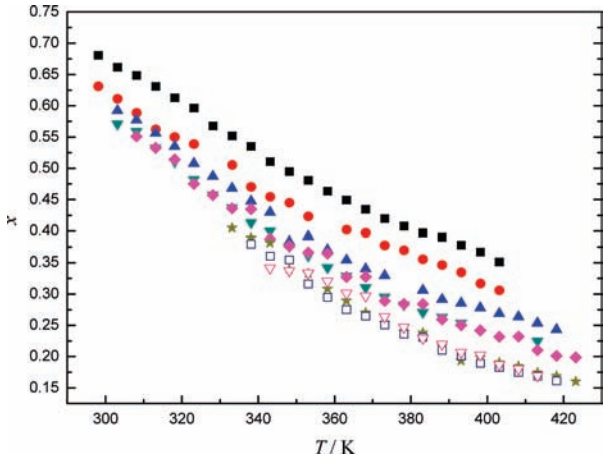

Figure 1. Mole fraction solubility x of SO_2 as a function of temperature in different mole ratios of caprolactam and tetrabutyl ammonium bromide: ■, 1:1; ●, 2:1; ▲, 3:1; ▼, 4:1; ◆, 5:1; ☆, 6:1; □, 7:1; ▽, 9:1.

Results and Discussions

Characterization of ILs. In this work, eight different mole ratios of caprolactam and tetrabutyl ammonium bromide ILs were synthesized and characterized. ^{1}H NMR spectra of caprolactam and tetrabutyl ammonium bromide (2:1) are presented. ^{1}H NMR (400 MHz, DMSO, δ): 7.4 ppm (*s*, 1H, **H**−N); 3.33 ppm to 3.17 ppm (*t*, 8H, $N^+(C\mathbf{H}_2)_4$); 3.06 ppm to 3.03 ppm (*t*, 2H, $HNC\mathbf{H}_2$); 2.29 ppm to 2.27 ppm (*t*, 2H, $OCC\mathbf{H}_2$); 1.67 ppm to 1.65 ppm (*t*, 2H, $OCCH_2-C\mathbf{H}_2$); 1.59 ppm to 1.56 ppm (*m*, 8H, $N^+(CH_2C\mathbf{H}_2)_4$); 1.54 ppm to 1.48 ppm (*t*, 4H, $OCCH_2CH_2C\mathbf{H}_2C\mathbf{H}_2$); 1.34 ppm to 1.29 ppm (*m*, 8H, $N^+(CH_2CH_2C\mathbf{H}_2)_4$); 0.94 ppm to 0.92 ppm (*t*, 12H, $N^+(CH_2CH_2CH_2C\mathbf{H}_3)_4$).

Effect of Temperature on the Solubility of SO_2 in ILs. The dissolution of SO_2 in the synthesized ILs was determined at (298.2 to 423.2) K and 101.3 kPa. The results are presented in Table 1 and more visually expressed in Figure 1. As can be observed, the solubility of SO_2 in different molarity CPL and TBAB decreases as both temperature and CPL composition in the systems increase.

The equilibrium solubilities of SO_2 in these eight ILs versus temperature at 101.3 kPa are presented in Figure 1. The mole fraction solubilities of SO_2 in these ILs decrease with the temperature increase. For example, the mole fraction solubility of SO_2 x in [CPL][TBAB] (1:1) is 0.680 at 298.2 K, while it decreases to 0.351 at 373.2 K. The mole fraction solubility of SO_2 in water is no more than 0.034 at 303.2 K and 0.0016 at 363.2 K.

Figure 1 shows the effect of CPL on the solubilities of SO_2. When the component of CPL increases, the solubilities of SO_2 decrease slowly. As an overall result of the different mole ratio of CPL and TBAB, [CPL][TBAB] (1:1, mole ratio) shows the highest capacity for absorption of SO_2, and the equilibrium concentration of SO_2 in it reaches a value of $x = 0.680$ at 298.2 K and 101.3 kPa. Therefore, [CPL][TBAB] (1:1, mole ratio) can be regarded as the most potential absorbent of SO_2 for flue gas desulfurization (FGD).

The change in solubility with temperature for the ILs in Figure 1 looks nonlinear. This nonlinear behavior has already been reported by several authors for pure ILs.[8−10,12] By increasing the composition of caprolactam in the systems, the temperature dependence becomes distinctly nonlinear, especially at high caprolactam content. As we all know, the gas solubility was negative correlation with temperature. A fifth-order polynomial

Table 2. Parameters of Equation 1 and rmsd of Equation 3 for SO_2 in [CPL][TBAB] ILs of Different Mole Ratio of Caprolactam and Tetrabutyl Ammonium Bromide

[CPL]:[TBAB]	a	b	$100c$	10^4d	10^7e	$10^{10}f$	10^3 rmsd
1:1	−1220	18.23	−10.84	3.207	−4.718	2.763	2.1
2:1	−4281	62.61	−36.53	10.63	−15.42	8.934	5.1
3:1	−675.0	10.07	−5.940	1.736	−2.511	1.440	2.0
4:1	2794	−39.75	22.58	−6.407	9.079	−5.138	2.1
5:1	1006	−14.29	8.108	−2.295	3.242	−1.826	7.8
6:1	4808	−60.41	30.28	−7.568	9.442	−4.704	5.3
7:1	62477	−832.5	443.1	−117.8	156.4	−82.94	3.9
9:1	−103422	1390	−745.8	199.8	−267.1	142.7	3.4

was found to satisfactorily correlate, from an empirical perspective, the change of solubility with temperature throughout the whole range of composition

$$x^{-1} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K})^3 + e(T/\mathrm{K})^4 + f(T/\mathrm{K})^5 \quad (1)$$

where T is for the absolute temperature and a, b, c, d, e, and f refer to the fit coefficients. The experimented solubility values of SO_2 (x_i) and calculated solubility values of SO_2 (x^{cacld}) are also given in Table 1. The values of the relative deviation (RD) are also given in Table 1. The RD is defined as eq 2.

$$\mathrm{RD} = \frac{|x_i - x_i^{\mathrm{calcd}}|}{x_i} \cdot 100 \quad (2)$$

where x_i^{calcd} represents the solubilities calculated from eq 1 and x_i represents the experimental values of solubility. The values of parameters a, b, c, d, e, and f and the root-mean-square deviations (rmsd) are listed in Table 2. The rmsd is defined as eq 3.

$$\mathrm{rmsd} = \left\{ \frac{\sum_{i=1}^{N} [(x_i^{\mathrm{calcd}} - x_i)^2]}{N} \right\}^{1/2} \quad (3)$$

where x is the mole fraction solubility of SO_2 in different temperature and mole ratio [CPL][TBAB] ILs; N is the number of experimental points; and the superscripts calcd and exptl refer to the values calculated from eq 1 and to the data for experimental solubilities, respectively.

Recycle of ILs. Both absorption and desorption of SO_2 gas in the three examined ILs (i.e., the mole ratio of CPL and TBAB is 1:1, 3:1, and 5:1) were relatively fast, providing complete absorption in 1 h with pure SO_2 gas (80 mL·min^{-1}, 200 rpm stirring) and complete gas desorption in 2 h at 373.2 K and 10.1 kPa vacuum. However, the absorption and desorption time are very dependent on the exposed surface area of the IL, thus making room for considerable improvement.

In Figure 2, six consecutive absorption cycles with the ILs were shown. There was little influence of using times of ILs on the solubility of SO_2. Moreover, the ILs could be reused six times without any loss of absorption capability.

Conclusions

A series of different mole ratios of CPL and TBAB ILs were synthesized. The mole fraction solubilities of SO_2 in the [CPL][TBAB] ILs at (298.2 to 403.2) K and atmospheric pressure were measured. The results of this work indicate that the solubility of SO_2 in [CPL][TBAB] ILs was high. The results show the mole fraction solubility increases with a decrease of temperature and the mole ratio of caprolactam. The experimental data were correlated by means of the fifth-order polynomial law.

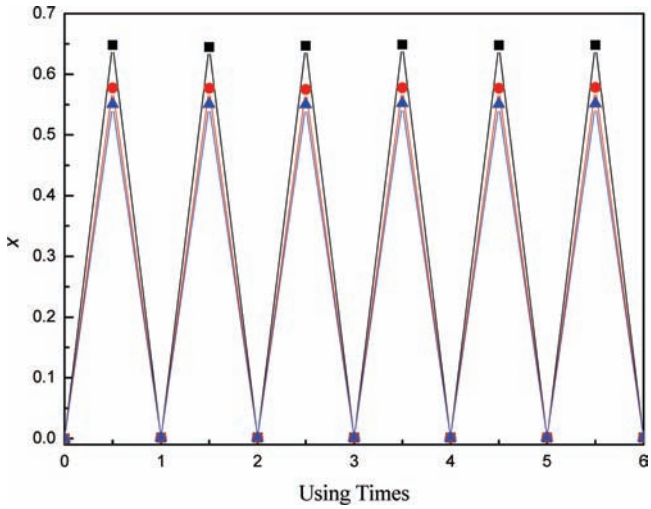

Figure 2. SO_2 desorption times by heating shown as mole fraction of SO_2 to different mole ratios of caprolactam and tetrabutyl ammonium bromide: ■, 1:1; ●, 3:1; ▲, 5:1.

The ILs could be reused. Therefore, the synthesized ILs show great potential as alternative solvents for the recovery of SO_2 in the industrial process of FGD.

Note Added after ASAP Publication: This paper was published ASAP on October 19, 2009. Temperature data in the abstract and the Results and Discussions section were corrected. The revised paper was reposted on January 22, 2010.

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