

# Efficient capture of SO<sub>2</sub> by a binary mixture of caprolactam tetrabutyl ammonium bromide ionic liquid and water

Erhong Duan<sup>a</sup>, Bin Guo<sup>a,\*</sup>, Miaomiao Zhang<sup>a</sup>, Yanan Guan<sup>a</sup>, Hua Sun<sup>b</sup>, Jing Han<sup>a</sup>

<sup>a</sup> School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, People's Republic of China

<sup>b</sup> College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, People's Republic of China

## ARTICLE INFO

### Article history:

Received 6 March 2011

Received in revised form 30 May 2011

Accepted 19 July 2011

Available online 5 August 2011

This paper is dedicated to the memory of Xiaowu.

### Keywords:

Caprolactam

Tetrabutyl ammonium bromide

Ionic liquids

SO<sub>2</sub>

Absorption

## ABSTRACT

The solubility of SO<sub>2</sub> in a binary mixture of water and caprolactam tetrabutyl ammonium bromide ionic liquid (CPL-TBAB IL) was investigated. Though the ionic liquid and water were fully miscible, a phase separation occurred when SO<sub>2</sub> was introduced into the mixture. The SO<sub>2</sub> concentrated in the lower layer, and it could be released by heating the solution under reduced pressure (382.2 K, 10.1 kPa). After desorption, the mixture could be reused to absorb SO<sub>2</sub>. It was found that SO<sub>2</sub> acts as a switch to cause the water and CPL-TBAB IL to phase separate, and the mechanics of this phase separation process was studied by gas chromatography–mass spectrometry, fourier transform-infrared spectroscopy and Karl–Fisher titration. The absorption and desorption of SO<sub>2</sub> in the CPL-TBAB/water mixtures were reversible.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

SO<sub>2</sub> emissions are a significant source of atmospheric pollution. When fossil fuels are combusted, SO<sub>2</sub> is produced; if these emissions escape into the atmosphere, they can cause the formation of acid rain, which is a serious environmental concern. Additionally, SO<sub>2</sub> emissions contribute to the formation of smog, which is a significant human health concern. If a practical process to selectively and reversibly absorb SO<sub>2</sub> could be identified, these emissions, along with their corresponding effects on the environment and human health, could be minimised. However, the identification of a material that can selectively and reversibly capture SO<sub>2</sub> has proven difficult.

Though SO<sub>2</sub> readily dissolves in water, upon dissolution, most of the SO<sub>2</sub> is converted to sulphurous acid; liberation of SO<sub>2</sub> occurs only upon heating. Aqueous solutions of liquid amines can react with SO<sub>2</sub> and trap it in the form of ammonium sulphite. However, when this process is employed on a large scale, the amines can evaporate into the gas stream due to their volatility. Furthermore, it is difficult to desorb the SO<sub>2</sub> from ammonium sulphite. A promising alternative is to use ionic liquids (ILs) to capture SO<sub>2</sub>. Ionic liquids are non-flammable and have desirable chemical and physical char-

acteristics, such as low volatilities, high thermal stabilities, and high solvation capacities [1–3]. Accordingly, new methods to synthesise [4] and apply [5–7] ILs have been the focus of a number of research groups. Recently, the removal of SO<sub>2</sub> from flue gas with ionic liquids has been the focus of experimental attention, but a practical method has yet to be identified. Thus, there is a demand to develop a process that can efficiently and absorb and reuse SO<sub>2</sub> from ionic liquids [8–16].

To this end, Huang prepared the 1,1,3,3-tetramethylguanidine (TMG)-based ILs, [TMG][BF<sub>4</sub>] and [TMG][Tf<sub>2</sub>N], which absorb a large amount of SO<sub>2</sub> gas. In these systems, the SO<sub>2</sub> does not undergo chemical transformation to a different species [8,9]. They also found that [BMIM][BF<sub>4</sub>] and [BMIM][Tf<sub>2</sub>N] could be used successfully for SO<sub>2</sub> gas absorption; however, these [BMIM] ILs were unable to separate SO<sub>2</sub> from N<sub>2</sub> gas mixtures. Wu has described a suitable methodology in which an IL derived from 1,1,3,3-tetramethylguanidinium lactate (TMGL) underwent reaction with SO<sub>2</sub> to form a guanidinium sulphurous acid cation; this IL was able to absorb 1 mol of SO<sub>2</sub> at 1 bar. The practical utility of this IL is limited because of its relatively low thermal stability, so only a fraction of the absorbed gas can be thermally released before degradation of the IL occurs [10]. Yuan has synthesised hydroxyl ammonium ionic liquids and observed that the solubility of SO<sub>2</sub> in tris-(2-hydroxyethyl) ammonium lactate was 0.4957 mol fraction. The solubility of SO<sub>2</sub> sharply decreased as the temperature increased [15]. Lee found that the solubility of SO<sub>2</sub> in ionic liquids varied in the

\* Corresponding author. Fax: +86 311 88632361.

E-mail address: [gbin69@163.com](mailto:gbin69@163.com) (B. Guo).

presence of different halide anions and that  $\text{SO}_2$  solubility increased in the presence of certain halide anions. The solubility of  $\text{SO}_2$  increased in the order of  $\text{Br} > \text{Cl} > \text{I}$ . It was proposed that the primary interaction of the halide occurs with the  $\text{C}_2\text{-H}$  of the imidazolium and the S atom of  $\text{SO}_2$  [17]. Luis noted that a membrane made of hydrophilic polyvinylidene fluoride and 1-butylimidazolium acetate ([BIM][Ace]) has different permeability values to different gases. Air had a permeability of  $6.29 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , while 10%  $\text{SO}_2$  in air had a permeability of  $33.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ .  $\text{CO}_2$  had a permeability of  $204.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The permeability of air is an order of magnitude lower than the  $\text{CO}_2$  permeability, and it is also lower than the permeability of 10%  $\text{SO}_2$  in air [18]. Shiflett developed a ternary equation of state (EOS) model for the  $\text{CO}_2/\text{SO}_2/1\text{-butyl-3-methylimidazolium methyl sulphate}$  ([BMIM][MeSO<sub>4</sub>]) system. The authors proposed that the enhanced selectivity of [BMIM][MeSO<sub>4</sub>] for  $\text{CO}_2$  over  $\text{SO}_2$  was significantly higher than 1-hexyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide ([HMIM][Tf<sub>2</sub>N]) [19,20]. Ren found that task-specific ILs could chemically absorb  $\text{SO}_2$  when the mole ratio of  $\text{SO}_2$  to the IL was less than 0.5; when the mole ratio was greater than 0.5, the IL could physically absorb  $\text{SO}_2$ . The normal ILs could only physically absorb  $\text{SO}_2$  [21]. We recently reported that caprolactam (CPL)-tetrabutyl ammonium bromide (TBAB) ionic liquid (CPL:TBAB = 1:1, mole ratio) has a high affinity for  $\text{SO}_2$  [22] (mole fraction solubility 0.680, 298.2 K) and a low affinity for diatomic gases like  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{S}$  [23]. However, the high viscosity (1500 mPas at 323.2 K) of the CPL-TBAB IL made mass and heat transfer difficult. The viscosity of the mixture of CPL-TBAB IL and water was very low.

The solubility of  $\text{SO}_2$  at different temperatures was determined in various compositions of CPL-TBAB IL and water. The viscosity of the ionic liquid/water mixtures was also measured. Based on the experimental solubility and viscosity data, two different formulas were proposed. The two phases that separate when  $\text{SO}_2$  is introduced into CPL-TBAB IL and water mixtures were characterised by fourier transform-infrared spectroscopy (FT-IR), gas chromatography–mass spectrometry (GC–MS) and Karl–Fisher titration, and the concentration of  $\text{SO}_2$  in each phase was measured. The mechanics of phase separation were studied, and the possibility of recycling the solutions was explored.

## 2. Experimental

### 2.1. Materials

The CPL-TBAB ionic liquid was synthesised as previously reported [22]. Ionic liquid aqueous solutions were prepared by mixing the ionic liquid and de-ionised water. The individual CPL-TBAB ionic liquid and water components were weighed using a balance with an uncertainty of  $\pm 0.0001 \text{ g}$ .  $\text{SO}_2$  with a purity of 99.9% was supplied by Beijing Analytical Instrument Factory.

### 2.2. The viscosity measurements

Viscosities of the binary mixtures were measured using LVDV-II+Pro viscometer, which was obtained from Brookfield-Instruments, US. Ultra Low Adapter (ULA) was used to increase accuracy. And the cover was used to prevent the evaporation of water. The temperature was controlled with a temperature accuracy of  $\pm 0.1 \text{ K}$ .

### 2.3. Absorption of $\text{SO}_2$ in mixtures of CPL-TBAB IL + water

The apparatus of absorption of  $\text{SO}_2$  in the mixtures of CPL-TBAB IL and water is shown in Fig. 1, which mainly consisted of a glass

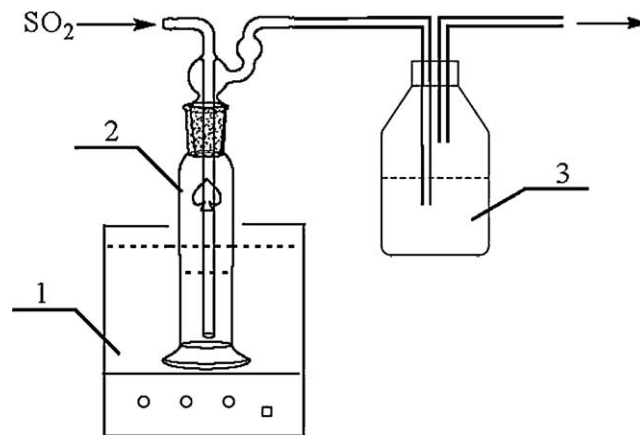


Fig. 1. Apparatus of absorption of  $\text{SO}_2$  using ionic liquids: 1 – water bath and magnetic stirrer; 2 – glass vessel; 3 – off-gas absorption.

vessel. The temperature was controlled by the water bath with a temperature accuracy of  $\pm 0.1 \text{ K}$ . Continuous stirring was achieved by the magnetic stirrer.  $\text{SO}_2$  gas was bubbled through predetermined amounts of the CPL-TBAB aqueous solutions (about 10 g) in glass vessels at a rate of  $10 \text{ mL min}^{-1}$ . Unabsorbed  $\text{SO}_2$  was neutralized with sodium hydroxide. The glass vessel was weighed using a balance with an uncertainty of  $\pm 0.0001 \text{ g}$  to get the mass of  $\text{SO}_2$  absorbed, through which the solubility of  $\text{SO}_2$  in the mixture can be calculated. The absorption concentration of  $\text{SO}_2$  in ILs versus time was determined at 298.2 K and 101.3 kPa, and that versus temperature was determined at 101.3 kPa and temperature from 293.2 K to 323.2 K. Considering the absorption rate, the equilibrium can be considered to be reached after 2 h in the thermodynamic experiments.

### 2.4. Recycling the CPL-TBAB IL

The two-phase mixture of CPL-TBAB, water, and  $\text{SO}_2$  (Fig. 2,  $L_1$  and  $L_2$ ) was separated using a separator funnel.  $L_1$  (the  $\text{SO}_2$ -enriched phase) and  $L_2$  were gained.  $\text{SO}_2$  was recycled from  $L_1$ . An oil bath, fitted with a temperature controller and a vacuum indicator, was used to heat  $L_1$  to release the  $\text{SO}_2$  and the little water. During the desorption process, the weight of  $L_1$  was periodically determined; experiments showed that the solubility of  $\text{SO}_2$  in  $L_1$  was close to zero at 383.2 K and 10.1 kPa vacuum. The binary mixture, caprolactam tetrabutyl ammonium bromide ionic liquid and water, of  $L_2$  and the residue of  $L_1$  recycled  $\text{SO}_2$  and little water was reformed. After added the appropriate amount of water, the aqueous solution of CPL-TBAB was again subjected to  $\text{SO}_2$  absorption (308.2 K, 101.3 kPa). When the mixture was saturated with  $\text{SO}_2$ , it was separated again.

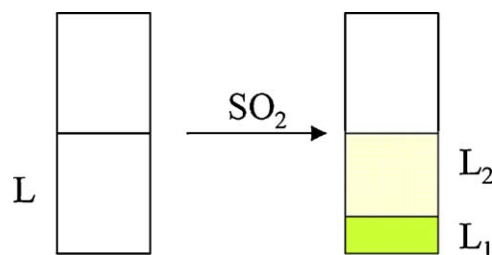


Fig. 2. Schematic of CPL-TBAB IL/water/ $\text{SO}_2$  phase behaviour.

**Table 1**  
Parameters for Eq. (1) and *R*-square values for the equilibrium solubility of SO<sub>2</sub> in pure CPL-TBAB IL and different concentrations of CPL-TBAB + water solutions with respect to temperature.

Entry	<i>a</i> (×10 <sup>-3</sup> )	<i>b</i> (×10 <sup>-1</sup> )	<i>c</i> (×10 <sup>2</sup> )	<i>d</i> (×10 <sup>4</sup> )	<i>R</i> <sup>2</sup>
0.1 mol L <sup>-1</sup>	1.200	-0.9734	2.629	-2360	0.998
1 mol L <sup>-1</sup>	-0.9500	1.105	-4.014	4671	0.999
2 mol L <sup>-1</sup>	5.747	-5.226	15.99	-1.643	0.999
3 mol L <sup>-1</sup>	8.010	-7.285	22.29	-2.289	0.999
4 mol L <sup>-1</sup>	6.548	-5.764	17.14	-1.718	1.000
CPL-TBAB IL	-5.556	6.142	-21.78	2.518	0.998

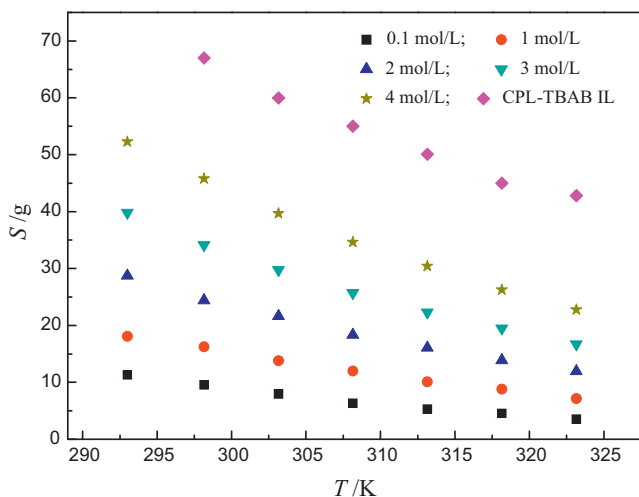
### 3. Results and discussion

#### 3.1. Effect of temperature on the solubility of SO<sub>2</sub> in CPL-TBAB IL + water solutions

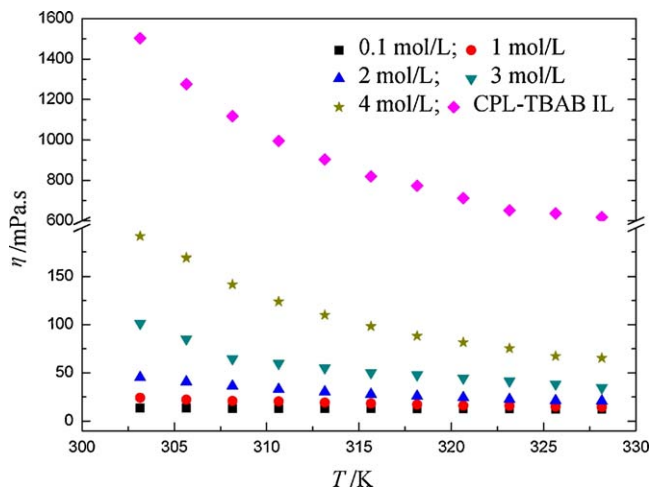
The equilibrium solubility (*S*, g/100 g solutions) of SO<sub>2</sub> in the pure CPL-TBAB IL, as well as in different compositions of CPL-TBAB and water, are presented in Fig. 3. The solubility of SO<sub>2</sub> in these solutions decreased sharply when the temperature was increased. The reason for SO<sub>2</sub> solubility relationship with temperature is very similar to the reason that vapor pressure increases with temperature. Increased temperature causes an increase in kinetic energy. The higher kinetic energy causes more motion in molecules which break intermolecular bonds and escape from solution. For instance, the solubility of SO<sub>2</sub> in the mixture of CPL-TBAB and water (4 mol L<sup>-1</sup>) was 52.29 g at 293.2 K and decreased to 22.75 g at 323.2 K. These solubility values are higher than that of 1,1,3,3-tetramethylguanidinium lactate [24] but lower than that of pure CPL-TBAB IL [22]. The solubility of SO<sub>2</sub> in these solutions increased when the concentration of CPL-TBAB IL was increased. The solubility of SO<sub>2</sub> in the CPL-TBAB solution (4 mol L<sup>-1</sup>) was higher than in pure water, which is due to the strong interaction between the CPL-TBAB IL and SO<sub>2</sub>. The viscosity of the CPL-TBAB and water solution was lower than that of the pure IL (Fig. 4). Therefore, the CPL-TBAB and water solutions (4 mol L<sup>-1</sup>) have excellent properties to efficiently capture SO<sub>2</sub>.

The solubility of SO<sub>2</sub> in the pure CPL-TBAB IL and in different compositions of CPL-TBAB/water solution appeared to be non-linear with respect to temperature (Fig. 3). For the purposes of comparison and application, the SO<sub>2</sub> solubility in these solutions was expressed as a function of temperature (Eq. (1)):

$$S/g = a + b(T/K) + c(T/K)^2 + d(T/K)^3 \quad (1)$$



**Fig. 3.** Solubility (*S*) of SO<sub>2</sub> in different concentrations of CPL-TBAB/water solutions and pure CPL-TBAB IL (*n*<sub>CPL</sub>/*n*<sub>TBAB</sub> = 2/1) as a function of temperature.



**Fig. 4.** Viscosity ( $\eta$ ) of the CPL-TBAB/water solutions and pure CPL-TBAB IL ( $n_{\text{CPL}}/n_{\text{TBAB}} = 2/1$ ) as a function of temperature.

In this equation, *S* represents the solubility value; *T* is the absolute temperature; and *a*, *b*, *c* and *d* refer to the fit coefficients. The values of the parameters *a*, *b*, *c*, *d* and *R*-square (*R*<sup>2</sup>) are listed in Table 1.

The viscosity of pure CPL-TBAB IL and CPL-TBAB and water solutions were determined with respect to temperature. These data were fit to an equation, which was first proposed by Vogel–Fulcher–Tammann (VFT) and subsequently used by other researchers (Eq. (2)) [25,26]. The fitted data are shown in Fig. 3.

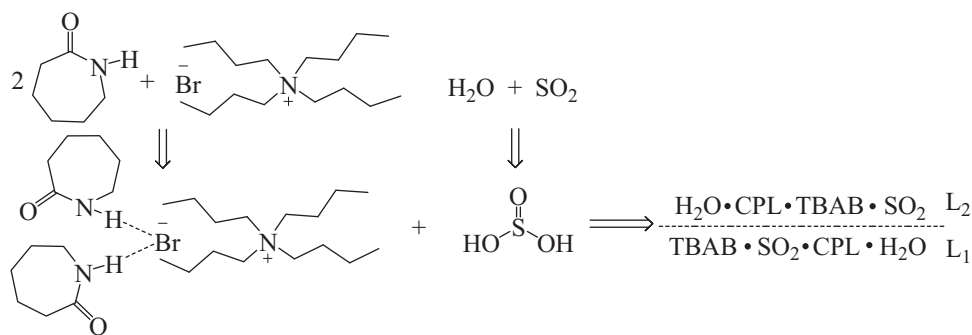
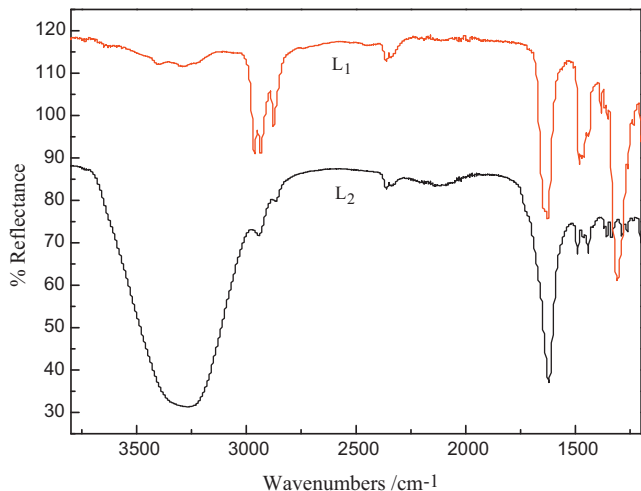
$$\eta/\text{mPa s} = A \cdot \exp \left\{ \frac{B}{(T/K) - T_0} \right\} \quad (2)$$

In this equation,  $\eta$  represents the viscosity value; *T* is the absolute temperature; and *A*, *B* and *T*<sub>0</sub> refer to the fit coefficients. The values of the parameters *A*, *B*, *T*<sub>0</sub> and *R*-square (*R*<sup>2</sup>) are listed in Table 2.

Water and the CPL-TBAB ionic liquid (2:1, mole ratio) were completely miscible at ambient conditions. However, when SO<sub>2</sub> was introduced into the mixture of the CPL-TBAB ionic liquid and water, a second liquid phase appeared; this process is represented in Fig. 4. This phenomenon is similar to what happens when CO<sub>2</sub> is added to ionic liquid/organic mixtures [27,28]. The densest phase was rich in CPL-TBAB IL and SO<sub>2</sub> (labelled *L*<sub>1</sub>), whereas the least dense phase was rich in water (labelled *L*<sub>2</sub>).

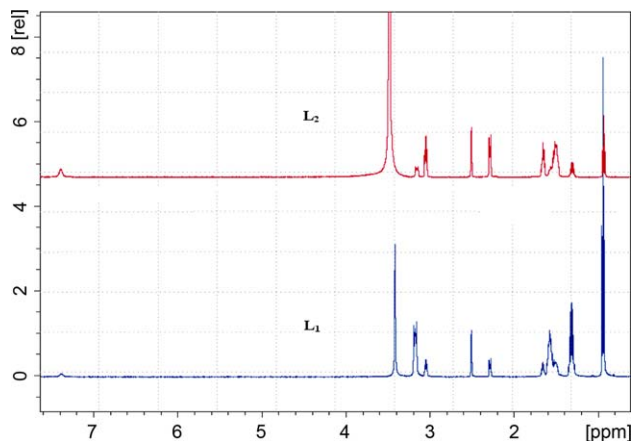
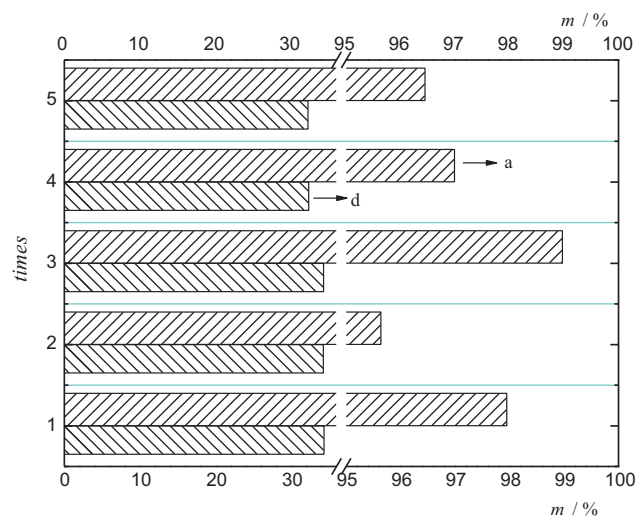
**Table 2**  
Parameters for Eq. (2) and *R*-square values for the viscosity measurements of pure CPL-TBAB IL and different concentrations of CPL-TBAB + water solutions with respect to temperature.

Entry	<i>A</i>	<i>B</i>	<i>T</i> <sub>0</sub>	<i>R</i> <sup>2</sup>
0.1 mol L <sup>-1</sup>	12.27	0.6391	297.26	0.858
1 mol L <sup>-1</sup>	11.17	12.56	287.84	0.952
2 mol L <sup>-1</sup>	14.89	14.27	291.23	0.962
3 mol L <sup>-1</sup>	29.16	10.02	295.66	0.957
4 mol L <sup>-1</sup>	42.11	19.17	291.50	0.960
CPL-TBAB IL	455.4	12.31	293.52	0.968

Scheme 1. Proposed reaction between CPL-TBAB, H<sub>2</sub>O and SO<sub>2</sub>.Fig. 5. FT-IR spectra of the layers from the CPL-TBAB IL/water/SO<sub>2</sub> system.

### 3.2. Characterisation of L<sub>1</sub> and L<sub>2</sub>

L<sub>1</sub> and L<sub>2</sub> were characterised by FT-IR spectroscopy (Fig. 5) and <sup>1</sup>H NMR (Fig. 6). As shown in Fig. 4, the O–H (H<sub>2</sub>O) and N–H (CPL) stretches (3400–3200 cm<sup>-1</sup>), C=O (CPL) stretch (1620 cm<sup>-1</sup>), N–H (CPL) bend (1490 cm<sup>-1</sup>), N–C–H (CPL) stretch (2960 and 2940 cm<sup>-1</sup>), and S=O (SO<sub>2</sub>) band (2360 and 2330 cm<sup>-1</sup>) were observed in L<sub>2</sub>. The N–C–H (CPL) stretch (2959, 2946 and 2922 cm<sup>-1</sup>), N<sup>+</sup>⋯H (TBAB) bend (1670 and 1470 cm<sup>-1</sup>) and S=O (SO<sub>2</sub>) band (2360 and 2330 cm<sup>-1</sup>) were found in L<sub>1</sub>. There is a large amount of H<sub>2</sub>O, some CPL and small quantities of TBAB and SO<sub>2</sub> in

Fig. 6. <sup>1</sup>H NMR spectra of the layers from the CPL-TBAB IL/water/SO<sub>2</sub> system.Fig. 7. SO<sub>2</sub> adsorption (mass percent) in CPL-TBAB/water (4 mol L<sup>-1</sup>) (a) and SO<sub>2</sub> desorption rate (mass percent) in L<sub>1</sub> (d) over five adsorption–desorption cycles.

L<sub>2</sub>. In L<sub>1</sub>, SO<sub>2</sub> and tetrabutylammonium bromide levels were high, and the level of caprolactam was low. Based on the NMR data, there was a trace amount of water in L<sub>1</sub>.

The SO<sub>2</sub>-saturated CPL-TBAB IL and water solution (4 mol L<sup>-1</sup>, 298.15 K) was characterised by thermal analysis (DTA), GC–MS and Karl–Fisher titration. The concentrations of CPL, TBAB, H<sub>2</sub>O and SO<sub>2</sub> in the two phases are shown in Table 3. From the data summarised in Table 3, it is clear that L<sub>1</sub> is enriched in SO<sub>2</sub>. There was a trace amount of water and caprolactam and a large amount of tetrabutylammonium bromide in L<sub>1</sub>.

### 3.3. Theoretical basis

The theoretical basis of this process was also investigated. Using the structure of (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>·2(NH<sub>2</sub>)<sub>2</sub>CS as a model [29–31], we propose that one CPL-TBAB IL molecule is formed from two CPL molecules and one TBAB molecule; this interaction is formed from two N–H⋯Br hydrogen bonds (Scheme 1). When SO<sub>2</sub> is added to the aqueous CPL-TBAB IL mixture, sulphurous acid is immediately formed. The N–H⋯Br hydrogen bond is broken, and a more stable O–H⋯Br hydrogen bond is formed at the same time

**Table 3**  
Concentration of CPL, TBAB, H<sub>2</sub>O and SO<sub>2</sub> in different phases.

Entry	n <sub>TBAB</sub> /mol	n <sub>CPL</sub> /mol	n <sub>H<sub>2</sub>O</sub> /mol	n <sub>SO<sub>2</sub></sub> /mol
L <sub>2</sub>	0.0108	0.209	1.98	0.0189
L <sub>1</sub>	0.103	0.0265	0.0210	0.511



[32,33]. This process is followed by formation of the triple hydrate ( $\text{SO}_2\text{-CPL/TBAB-H}_2\text{O}$ ). When the concentration of  $\text{SO}_2$  is increased, the CPL-TBAB IL and water solution separates into two layers ( $L_1$  and  $L_2$ ). The  $\text{SO}_2$  is concentrated in the lower phase ( $L_1$ ).

#### 3.4. Reusability of CPL-TBAB ILs

After the two layers ( $L_1$  and  $L_2$ ) were separated, the  $\text{SO}_2$  was removed from  $L_1$  by heating under reduced pressure (383.2 K, 10.1 kPa). The composition of the regenerated mixture was almost identical to that of the original solution, except that a small amount of water was lost. The results of five consecutive absorption–desorption cycles with the ILs–water solution are shown in Fig. 7. The performance of the IL and water mixture did not significantly change after repeated absorption–desorption cycles.

#### 4. Conclusion

The solubility (g/100 g solutions) of  $\text{SO}_2$  in CPL-TBAB/water ( $4\text{ mol L}^{-1}$ ) is 52.29 at 293.2 K. CPL-TBAB ionic liquid and water can completely miscible in all proportions at ambient conditions; the second phase appears along with the  $\text{SO}_2$  is introduced into the solution.  $\text{SO}_2$  could be a separation switch for water and the caprolactam-tetrabutyl ammonium bromide ionic liquid. The intermolecular forces in the triple hydrate ( $\text{SO}_2\text{-CPL/TBAB-H}_2\text{O}$ ) are larger than the intermolecular forces between  $\text{SO}_2$  and water, and the solubility of  $\text{SO}_2$  in the binary system is higher than that of water. Moreover,  $\text{SO}_2$  could be easily liberated from the triple hydrate ( $\text{SO}_2\text{-CPL/TBAB-H}_2\text{O}$ ). Thus, the binary system of CPL-TBAB IL and water is a more suitable solvent than water alone for the removal of  $\text{SO}_2$  from flue gas. The thermodynamic data show that the CPL-TBAB IL and water solutions can be used to sequentially absorb and release  $\text{SO}_2$ . The released  $\text{SO}_2$  is easy to reuse. The kinetics and theory of this process will be studied in the near future.

#### Acknowledgement

This research is supported by Hebei University of Science and Technology (XL201022 and QD201014).

#### References

- [1] R.K. Rogers, K.R. Seddon, *Ionic Liquids: Industrial Applications to Green Chemistry*, American Chemical Society, Washington, DC, 2002.
- [2] J.D. Holbrey, W.M. Reichert, R.G. Reddy, R.D. Rogers, *Ionic Liquids as Green Solvents: Progress and Prospects*, American Chemical Society, Washington, DC, 2003.
- [3] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis,  $\text{CO}_2$  capture by a task-specific ionic liquid, *J. Am. Chem. Soc.* 124 (2002) 926–927.
- [4] C. Chiappa, P. Piccooli, D. Pieraccini, Selective N-alkylation of anilines in ionic liquids, *Green Chem.* 8 (2006) 277–281.
- [5] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: recent progress from knowledge to applications, *Appl. Catal. A: Gen.* 373 (2010) 1–5.
- [6] P. Kubisa, Application of ionic liquids as solvents for polymerization processes, *Prog. Polym. Sci.* 29 (2004) 3–12.
- [7] D. Wei, A. Ivaska, Applications of ionic liquids in electrochemical sensors, *Anal. Chim. Acta* 607 (2008) 126–135.
- [8] J. Huang, A. Riisager, W.B. Rolf, Tuning ionic liquids for high gas solubility and reversible gas sorption, *J. Mol. Catal. A: Chem.* 2 (2008) 170–176.
- [9] J. Huang, A. Riisager, P. Wasserscheid, R. Fehrmann, Reversible physical absorption of  $\text{SO}_2$  by ionic liquids, *Chem. Commun.* 38 (2006) 4027–4029.
- [10] W.Z. Wu, B.X. Han, H.X. Gao, Z.M. Liu, T. Jiang, J. Huang, Desulfurization of flue gas:  $\text{SO}_2$  absorption by an ionic liquid, *Angew. Chem. Int. Ed.* 18 (2004) 2415–2417.
- [11] D. An, L.B. Wu, S.P. Zhu, Synthesis and  $\text{SO}_2$  absorption/desorption properties of poly(1,1,3,3-tetramethylguanidine), *Macromolecules* 9 (2007) 3388–3393.
- [12] Y. Wang, H.H. Pan, H.R. Li, C. Wang, Force field of the TMGL ionic liquid and the solubility of  $\text{SO}_2$  and  $\text{CO}_2$  in the TMGL from molecular dynamics simulation, *J. Phys. Chem. B* 35 (2007) 10461–10467.
- [13] Y. Wang, C. Wang, L.Q. Zhang, H.R. Li, Difference for  $\text{SO}_2$  and  $\text{CO}_2$  in TMGL ionic liquids: a theoretical investigation, *Phys. Chem. Chem. Phys.* 10 (2008) 5976–5982.
- [14] J.L. Anderson, J.K. Dixon, E.J. Maginn, J.F. Brennecke, Measurement of  $\text{SO}_2$  solubility in ionic liquids, *J. Phys. Chem. B* 31 (2006) 15059–15062.
- [15] X.L. Yuan, S.J. Zhang, X.M. Lv, Hydroxyl ammonium ionic liquids: synthesis, properties and solubility of  $\text{SO}_2$ , *J. Chem. Eng. Data* 2 (2007) 596–599.
- [16] Y.Y. Jiang, Z. Zhou, Z. Jiao, L. Li, Y.T. Wu, Z.B. Zhang,  $\text{SO}_2$  gas separation using supported ionic liquid membranes, *J. Phys. Chem. B* 19 (2007) 5058–5061.
- [17] K.Y. Lee, C.S. Kim, H. Kim, M. Cheong, D.K. Mukherjee, K.D. Jung, Effects of halide anions to absorb  $\text{SO}_2$  in ionic liquids, *Bull. Korean Chem. Soc.* 31 (2010) 1937–1940.
- [18] P. Luis, L.A. Neves, C.A.M. Afonso, I.M. Coelho, J.G. Crespo, A. Garea, A. Irbien, Facilitated transport of  $\text{CO}_2$  and  $\text{SO}_2$  through supported ionic liquid membranes (SILMs), *Desalination* 245 (2009) 485–493.
- [19] M.B. Shiflett, A. Yokozeki, Chemical absorption of sulfur dioxide in room-temperature ionic liquids, *Ind. Eng. Chem. Res.* 49 (2010) 1370–1377.
- [20] M.B. Shiflett, A. Yokozeki, Separation of carbon dioxide and sulfur dioxide using room-temperature ionic liquid [bmim][MeSO<sub>4</sub>], *Energ. Fuel* 24 (2010) 1001–1008.
- [21] S. Ren, Y. Hou, W. Wu, Q. Liu, Y. Xiao, X. Chen, Properties of ionic liquids absorbing  $\text{SO}_2$  and the mechanism of the absorption, *J. Phys. Chem. B* 114 (2010) 2175–2179.
- [22] B. Guo, E.H. Duan, A.L. Ren, Y. Wang, H.Y. Liu, The solubility of  $\text{SO}_2$  in caprolactam tetrabutyl ammonium bromide ionic liquids, *J. Chem. Eng. Data* 55 (2010) 1398–1401.
- [23] B. Guo, E.H. Duan, Y.F. Zhong, L. Gao, X.S. Zhang, D.S. Zhao, Absorption and oxidation of  $\text{H}_2\text{S}$  in caprolactam tetrabutyl ammonium bromide ionic liquid, *Energ. Fuel* 25 (2011) 159–161.
- [24] W.Z. Wu, B.X. Han, H.X. Gao, Z.M. Liu, T. Jiang, J. Huang, Desulfurization of flue gas:  $\text{SO}_2$  absorption by an ionic liquid, *Angew. Chem. Int. Ed.* 43 (2004) 2415–2417.
- [25] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate and 1-methyl-3-octylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 51 (2006) 1161–1167.
- [26] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, *J. Chem. Eng. Data* 52 (2007) 1080–1085.
- [27] A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke,  $\text{CO}_2$  as a separation switch for ionic liquid/organic mixtures, *J. Am. Chem. Soc.* 124 (2002) 10276–10277.
- [28] B.R. Mellein, J.F. Brennecke, Characterization of the ability of  $\text{CO}_2$  to act as an antisolvent for ionic liquid/organic mixtures, *J. Phys. Chem. B* 18 (2007) 4837–4843.
- [29] M. Shi, J.N. Zhang, Q. Li, Tetra-*n*-butylammonium bromide-thiourea (1/2), a layer-type inclusion compound, *J. Chem. Crystallogr.* 11 (2003) 831–837.
- [30] W. Lin, A. Delahaye, L. Fournaison, Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of  $\text{CO}_2$  + TBAB, *Fluid Phase Equilib.* 264 (2008) 220–227.
- [31] J. Lipkowski, V.Y. Komarov, T.V. Rodionova, Y.A. Dyadin, L.S. Aladko, The structure of tetrabutylammonium bromide hydrate ( $\text{C}_4\text{H}_9$ )<sub>4</sub>NBr·21/3H<sub>2</sub>O, *J. Supramol. Chem.* 2 (2002) 435–439.
- [32] K. Yasushi, Y. Yukiyasu, E. Takao, O. Hiroyuki, S. Wataru, N. Hideo, Hydrogen sulfide separation using tetra-*n*-butyl ammonium bromide semi-clathrate (TBAB) hydrate, *Energ. Fuel* 19 (2005) 1717–1722.
- [33] S. Fan, S. Li, J. Wang, X. Lang, Y. Wang, Efficient capture of  $\text{CO}_2$  from simulated flue gas by formation of TBAB or TBAF semiclathrate hydrates, *Energ. Fuel* 23 (2009) 4202–4208.