



Capture of Sulphur Dioxide by Hydroxyl Ammonium Ionic Liquid-DBU Mixtures

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Three hydroxyl ammonium ionic liquids containing the alcoholic hydroxy group were synthesized that mixed with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to form integrated sorption systems with the mole ratio of 1:1. At ambient temperature and atmospheric pressure, the absorption of SO₂ by integrated ionic liquid-DBU systems was investigated. The saturated absorption mole ratio of SO₂/ILs was 0.30, 0.50 and 0.66, respectively. And that of SO₂/ILs-DBU was 2.63, 2.83 and 2.96, respectively. The net increase in the saturated absorption mole ratio of three mixed absorption systems was close to 2.3 after deducting the SO₂ saturated absorption capacity of pure ionic liquids. The results indicated that SO₂ was absorbed fastly and efficiently by the mixed systems and the absorption could be completed in 0.5 h. In addition, the mixed systems had a strong regenerative ability. It's absorption capacity and rate were hardly changed after four SO₂ absorption-desorption cycle experiments.

Keywords: Hydroxyl ammonium ionic liquids, 1,8-Diazabicyclo[5.4.0]undec-7-ene, Sulphur dioxide, Absorption.

INTRODUCTION

With the rapid development of the economic globalization, the demand and consumption of fossil fuels are soaring. The SO₂ pollution, which would lead to the formation of acid rain and smog, caused by coal-combustion has become the most pollution factor in atmospheric environment and achieves extensively attention all over the world. Up to now, flue gas desulphurization is considered as one of the most effective ways to control emissions of SO₂. Although there are some commercial flue-gas desulphurization (FGD) ways including wet FGD, semidry FGD and dry FGD processes which are widely used in industrial desulphurization. There still exist some inherent drawbacks in desulphurization processes, such as the waste byproducts, corrosion of equipment, the difficulty to recycle SO₂ and the secondary pollution. So the most attractive approach for the separation of SO₂ from the flue gas stream is that SO₂ can be absorbed selectively and then released from saturated absorption solution by some measures. In recent years, many room temperature ionic liquids (RTILs) have been proposed as alternative absorbent for SO₂¹⁻¹⁰ for their negligible vapor pressure, miniscule flammability, high thermal and chemical stability. The room temperature ionic liquids used so far for SO₂ separation mainly including the hydroxyl-ammonium-based ionic liquids^{5,6} and tetramethylguanidinium-based ionic liquids (ILs) such as [TMG]¹, PTMGA¹⁰, [TMG][BF₄]^{2,3} and [TMG][BTA]². Although the hydroxyl-

ammonium-based ionic liquids in these ionic liquids are low cost than others, their absorption capacity is usually lower than other ionic liquids and the time required for reaching equilibrium is relatively longer.

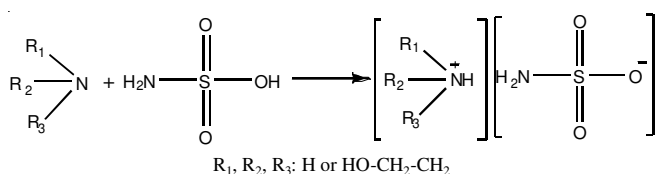
Recently, a novel class reversible of CO₂^{11,12} and SO₂¹³ binding organic liquids (CO₂BOL and SO₂BOL) which are liquid mixture of an hydroxyl compounds and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (amidine, guanidine) based on the reactions of CO₂, SO₂ and DBU reported. In this mixed absorption system, adding DBU in hydroxyl ammonium ionic liquids can not only largely increase the absorption capacity of absorbent to target gas, but also remain the original equilibrium time. Herein, we report a new organic sulphur-bearing ionic liquid system which is composed of the relative low cost hydroxyl ammonium ionic liquids and DBU.

EXPERIMENTAL

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aladdin reagent Co., Ltd. Sulphur dioxide (99.9 %) was supplied by Dalian Date Special Gas Co., Ltd. Triethanolamine (AR grade, purity ≥ 98 %) was purchased from Tianjin Bodi Chemical Reagent Co., Ltd. Diethanolamine (AR grade, purity ≥ 99 %) was purchased from Chengdu Kelong Chemical Reagent Co., Ltd. Sulfamic acid (AR grade, purity ≥ 99.5 %) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Co., Ltd. 2-Aminoethanol was purchased from Tianjin Fengfan Chemical Reagent Co., Ltd. All other chemicals were

purchased from commercial suppliers and were of the highest purity available.

Synthesis of ionic liquids: Hydroxyl ammonium ionic liquids were prepared by direct neutralization of alkanolamine and sulfamic acid. As an example, the synthesis procedure of *tris*-(2-hydroxyethylammonium) sulphamate is proposed here: 9.71 g (0.1 mol) sulfamic acid was added into a 150 mL flask and then a slight excess of an equimolar triethanolamine was transferred to the flask. The solution was stirred vigorously to mix well by a magnetic stirrer for approximately 24 h at 298.15 K and 101 kPa. The resulting liquid was collected and washed with ethanol (3×20 mL). A colourless product was obtained after evaporation and dried under vacuum at 353.15 K for 24 h. The synthesized reaction for ionic liquids is expressed in Scheme-I.



Scheme-I: Synthesized reaction of hydroxyl ammonium ionic liquids

Characterization of ionic liquids: The structure of synthesized ionic liquids was determined by IR and NMR characterization. IR spectra was obtained on a BioRad FTS-40 infrared spectrophotometer, 1H NMR spectra was recorded on a Bruker DRX 500-MHz spectrometer, using DMSO as solvent with TMS as internal standard.

Absorption capacity determination: The selected mixed adsorption systems were composed of DBU and different ionic liquids with the molar ratio of 1:1. The pure ionic liquids and ILs-DBU absorption solution were loaded into absorber, while dry SO_2 was passed into the reactor under atmospheric pressure.

RESULTS AND DISCUSSION

Effect of time on absorption capacity: Sulphur dioxide was absorbed by pure ionic liquids. Three reactions with different ionic liquids all reached equilibrium state after about 0.5 h and the saturated absorption mole ratio of SO_2 /ILs was 0.30, 0.50 and 0.66, respectively. Fig. 1 showed, the order of mixed absorption systems on the SO_2 adsorption capacity was: *tris*-(2-hydroxyethylammonium)sulfamate > *bis*-(2-hydroxyethylammonium)sulfamate > 2-hydroxyethylammonium sulfamate and the absorption capacity increased with the basicity increase in the cation.

Sulphur dioxide was absorbed by ILs-DBU mixed absorption solution. Three mixed absorption systems reached the equilibrium state about 0.5 h and the saturated absorption mole ratio of SO_2 /ILs-DBU was 2.63, 2.83 and 2.96, respectively. Fig. 2 showed the order of mixed absorption systems on the SO_2 adsorption capacity was: *tris*-(2-hydroxyethylammonium)sulfamate-DBU > *bis*-(2-hydroxyethylammonium)sulfamate-DBU > 2-hydroxyethylammonium sulfamate-DBU. The result showed that adding DBU can not only remain the time to reach equilibrium at 0.5 h, but also increase the absorption capacity greatly.

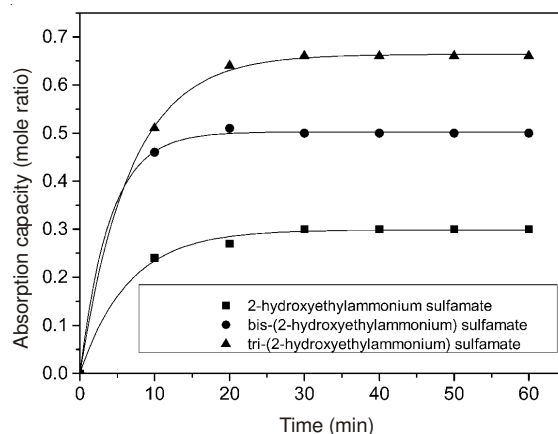


Fig. 1. Mole ratio of SO_2 /ILs as a function of time

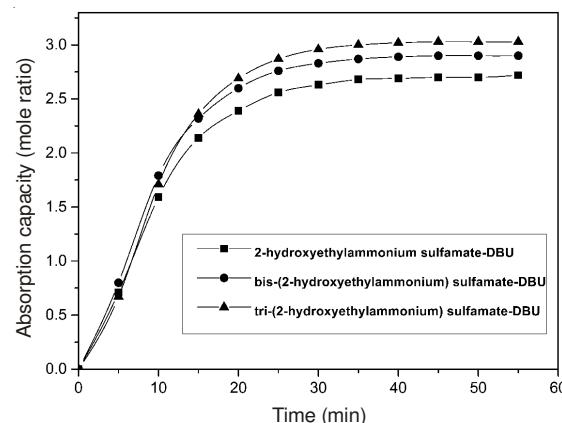


Fig. 2. Mole ratio of SO_2 /ILs-DBU as a function of time

Effect of temperature on absorption capacity: The variation of adsorption capacity of ionic liquids with temperature was presented in Fig. 3. It could be seen that the solubility of SO_2 in three ionic liquids decreased with the increase of temperature. The variation of adsorption capacity of ILs-DBU with temperature was presented in Fig. 4. It could be seen that the solubility of SO_2 in three mixed absorption systems decreased sharply with increasing temperature. This phenomenon indicated that the SO_2 desorption could be released by heating.

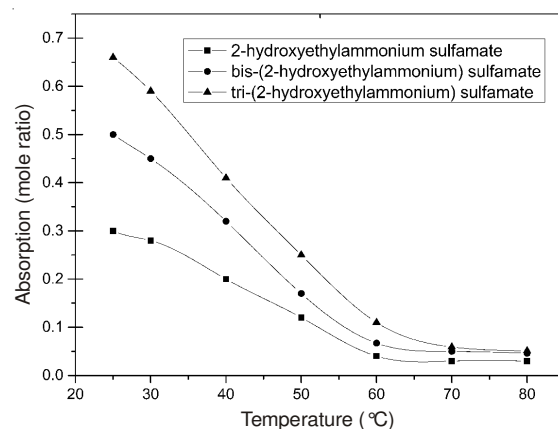


Fig. 3. Mole ratio of SO_2 /ILs as function of temperature

Due to the hydroxyl ammonium ionic liquids with a little solubility for SO_2 , the absorption mole ratio of SO_2 which has been absorbed by alcoholic hydroxyl and DBU in mixed

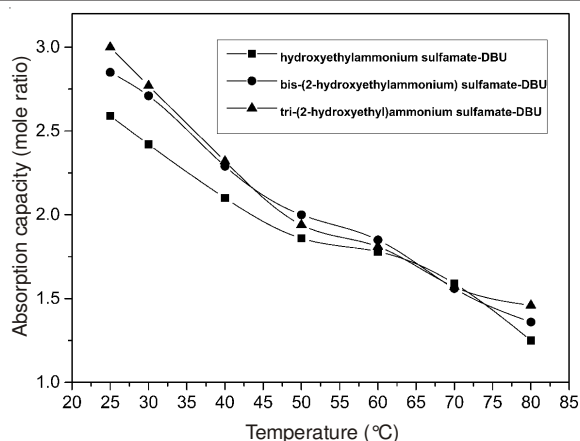


Fig. 4. Mole ratio of $\text{SO}_2/\text{ILs-DBU}$ as a function of temperature

absorption systems was equal to that of $\text{SO}_2/\text{ILs-DBU}$ subtracting the SO_2 absorption capacity of pure ionic liquids. Fig. 5 showed that after deducting the SO_2 saturated absorption capacity of pure ionic liquids, it could be calculated that the saturated absorption mole ratio of $\text{SO}_2/\text{ILs-DBU}$ separately was 2.33, 2.33, 2.30 and the absorption capacity didn't have any visibly growth as the increase of alcoholic hydroxyl group in ionic liquids.

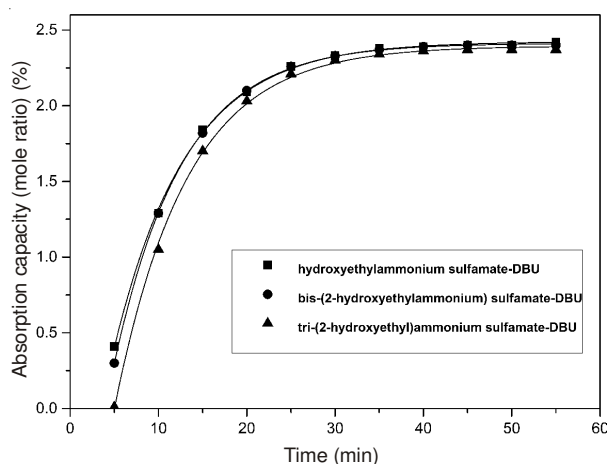


Fig. 5. Mole ratio of $\text{SO}_2/\text{ILs-DBU}$ deducting the mole ratio of SO_2/ILs as a function of time

Mechanism of absorption: The saturated absorption mole ratio of three mixed absorption systems was close to 2.3 after deducting the SO_2 saturated absorption capacity of pure ionic liquids. It was similar to the phenomenon that sulphur dioxide absorbed by *n*-hexyl alcohol-DBU absorption solution reported in literature¹³. It indicated that the chemical reaction occurs in the ILs-DBU mixed system which including sulphur dioxide with alcoholic hydroxyl and DBU.

In order to gain a further understanding of the absorption mechanism, 2-hydroxyethylammonium sulfamate was characterized by IR and NMR spectrum before and after capturing SO_2 . From Fig. 6, it can be seen that IR spectrum of 2-hydroxyethylammonium sulfamate didn't generate new absorption peaks before and after capturing SO_2 . ^1H NMR spectrum (Fig. 7) of 2-hydroxyethylammonium sulfamate didn't emerge new chemical shifts except 3.3 ppm water peak before and after capturing SO_2 . So the results indicated that 2-hydroxyethyl-

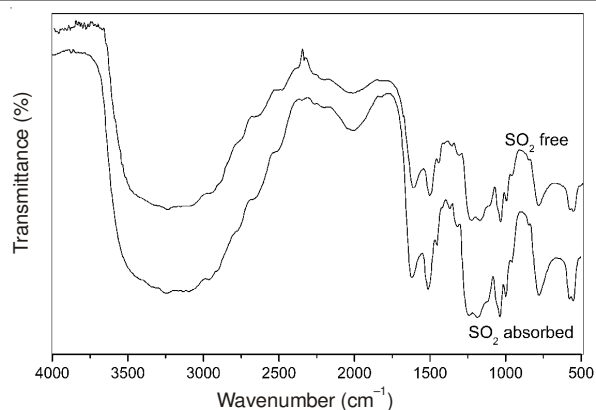


Fig. 6. IR spectrum of the 2-hydroxyethylammonium sulfamate ionic liquid before and after capturing SO_2

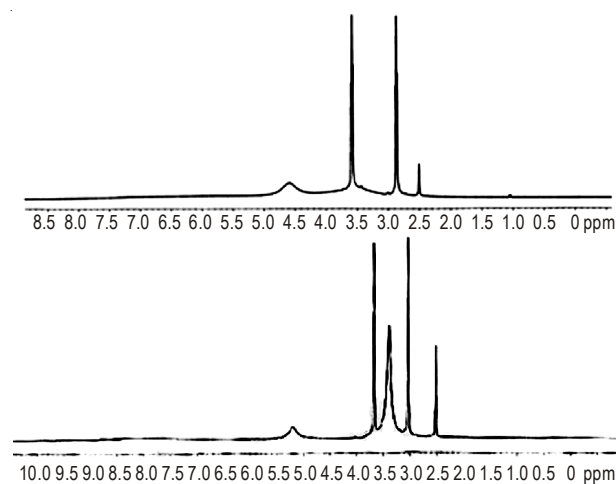


Fig. 7. ^1H NMR spectra of the 2-hydroxyethylammonium sulfamate ionic liquid before and after capturing SO_2

ammonium sulfamate for capturing SO_2 was purely physical absorption.

2-Hydroxyethylammonium sulfamate-DBU was characterized by NMR spectrum before and after capturing SO_2 . The ^1H NMR spectrum in Fig. 8 showed that three new resonance peaks were found in $\delta = 7.73, 9.54$ and 9.89 ppm and the chemical shift at $\delta = 9.89$ ppm was generated by the heterocyclic hydrogen (H-N=C) in DBU. Combined with the ^1H NMR spectrum of 2-hydroxyethylammonium sulfamate-DBU (Fig. 9), the resonance peak at $\delta = 4.24$ ppm which was produced by $-\text{NH}_2$ and $-\text{OH}$ was disappeared. When SO_2 was passed into the absorption system, the H in alcoholic hydroxyl would dissociate and integrate with N atom in the DBU ring where contains the isolated electron pair. So it leads to the formation of conjugate-structure in DBU ring. Thus, the new resonance peak at $\delta = 9.89$ ppm was consistent with nitrogen atom in the protonated DBU heterocyclic. The dissociation of H in alcoholic hydroxyl weakened the effect of intra molecular hydrogen bond and the chemical shift in NH_2 downfield shifted to $\delta = 7.73$ ppm. Because the active hydrogen atom in $-\text{NH}_3^+$ shifted to N atom in the DBU ring, resulting in the formation of N-H bond and the new resonance peak at 9.54 ppm.

Based on previous reports and above results, we proposed the reaction mechanism between SO_2 and the mixed absorption system consisted of the alcoholic hydroxyl group and DBU, which was shown in **Scheme-II**.

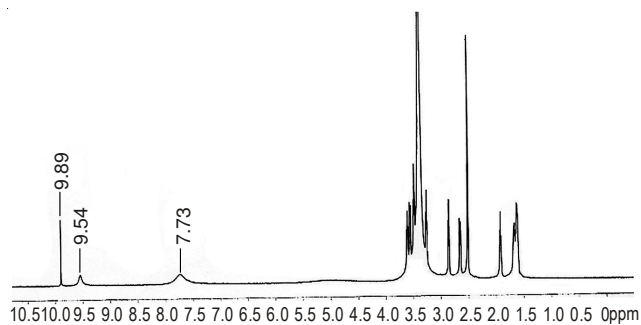


Fig. 8. ^1H NMR spectrum of the 2-hydroxyethylammonium sulfamate ionic liquid-DBU- SO_2

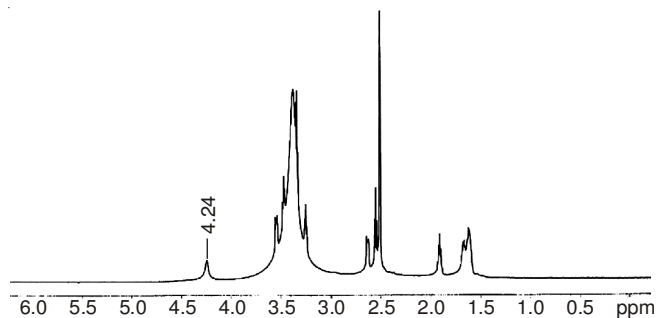
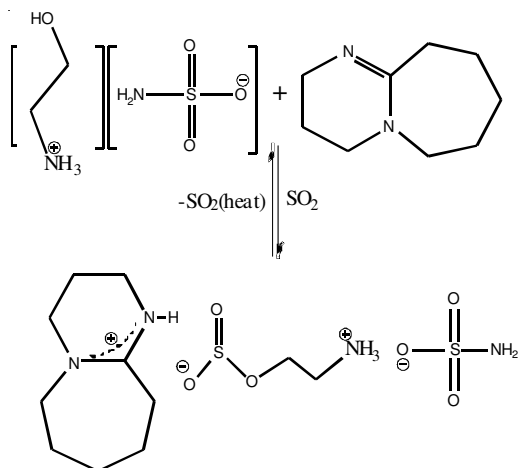


Fig. 9. ^1H NMR spectrum of the 2-hydroxyethylammonium sulfamate ionic liquid-DBU



Scheme-II: Reaction mechanism between the hydroxyl ammonium ionic liquid-DBU and SO_2

Thermal stability: The thermal behaviour of 2-hydroxyethylammonium sulfamate was determined by DTA and TGA. The heating rate and final temperature of is $5\text{ }^\circ\text{C}/\text{min}$ and $800\text{ }^\circ\text{C}$, respectively. Fig. 10 shows the DTA and TGA curves of 2-hydroxyethylammonium sulfamate from $25\text{--}800\text{ }^\circ\text{C}$. It indicated that 2-hydroxyethylammonium sulfamate was stable up to $280\text{ }^\circ\text{C}$ and decomposed rapidly over $300\text{ }^\circ\text{C}$.

Recycling of ionic liquids: In order to investigate the stability of SO_2 -saturated mixed absorption systems which were composed of hydroxyl ammonium ionic liquids and DBU, we chose one SO_2 -saturated mixed absorption system which was composed of 2-hydroxyethylammonium sulfamate ionic liquid and DBU, to conduct SO_2 absorption-desorption cycle experiments. After the desorption cycle experiments, it showed that it was difficult to absorb 1 mole SO_2 from absorption solution, because SO_2 molecules were bonded with alcohol

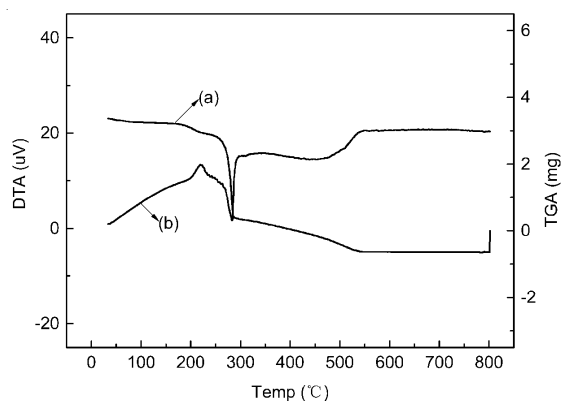


Fig. 10. TGA and DTA curves of 2-hydroxyethylammonium sulfamate ionic liquid. The curve of TGA is (a) and the curve of DTA is (b)

hydroxyl and formed new ionic liquids. From Fig. 11, it could be seen that SO_2 absorption capacity and absorption rate were hardly changed in four SO_2 absorption-desorption cycle experiments. It indicated that the new ionic liquid had good stability and could be recycled.

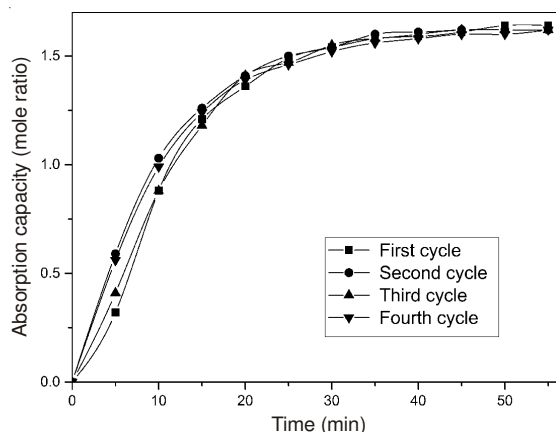


Fig. 11. Four consecutive cycles of SO_2 absorption and desorption in 2-hydroxyethylammonium sulfamate ionic liquid

Comparison of SO_2 absorption performance for different ionic liquids: In recent years, it was discovered that some new alcohol amine ionic liquids have better effectiveness for SO_2 gas absorption and desorption from a large number of experiments and research. The 1,1,3,3-tetramethyl guanidine lactic acid salt ionic liquid was synthesized by Wu, *et al.*¹ and it was applied for absorbing SO_2 at atmospheric pressure and $40\text{ }^\circ\text{C}$, meanwhile SO_2 could be desorbed after heating or vacuum desorption. Wu *et al.*¹⁴ have prepared the novel porous cross-linking particles with 1,1,3,3-tetramethyl guanidine lactate salt and N,N-methylene bisacrylamide successfully and the study for absorption and desorption of SO_2 indicated that it possessed higher efficiency and absorption capacity for SO_2 . A series of 1,1,3,3-tetramethyl guanidine ionic liquids were synthesized and studied by Riisager *et al.*⁷ and the result showed that SO_2 can be fully desorbed under the conditions of high temperature and low pressure. A series of alkaline liquids was synthesized by the reaction of alcohol amine with acid, lactic acid or structure similar acids at room temperature by Zhang *et al.*^{5,15-17}, using the pure ionic liquids or supported on the carrier have possessed more high absorption efficiency

and less short equilibration time at ambient temperature and atmospheric pressure. The principle of the absorption and desorption SO_2 of the alcohol amine ionic liquids were characterized by ^1H NMR and the recycling study of ionic liquids was carried out.

This study indicated that the mechanism of alcohol amine ILs-DBU absorption for SO_2 existed both physical and chemical absorption, because SO_2 was absorbed in the ionic liquid by physical absorption, then the amino group active positions reacted with ethanolamine cation easily. The result showed that the alcohol amine ILs-DBU system had better absorption capacity for SO_2 . We raised an assumption that the mechanism was typical chemical absorption, exactly showed in **Scheme-II**.

However, this chemical bond was relatively weak, which can be easily broken at high temperatures. The physical adsorption of SO_2 can be desorbed at high temperatures easily. Thus, the desorption of SO_2 will be easier and more complete at the higher temperature, which results in shorter desorption time and higher desorption rate.

The saturated absorption mole ratio of SO_2 /ILs-DBU was close to 2.3 according to the above description. From **Scheme-II**, it can be seen that we attribute 1 equivalent of 2.3 equivalents of SO_2 to bind with the alcoholic hydroxyl group and DBU, then about 1.3 equivalents of SO_2 physically was dissolved in newly generated complex sulphur-bearing ionic liquids. When SO_2 firstly dissolved in hydroxyl ammonium ILs-DBU in purifying SO_2 experiments, the viscosity of the absorption solution increased markedly, it made the agitation more difficult, but the absorption solution remained colourless. With more and more SO_2 dissolved in absorption solution, the viscosity of absorption solution reduced gradually, so it made the agitation more readily. The phenomenon of change in viscosity resulted from the changes of absorption property was consistent with reported in literature³.

Conclusion

The absorption system including DBU and ionic liquid containing alcoholic hydroxyl had high absorption capacity for SO_2 . Adding DBU in hydroxyl ammonium ionic liquids didn't only remain the original equilibration time which was got while ionic liquids containing alcoholic hydroxyl absorb SO_2 , but also improved largely absorption capacity for SO_2 .

Combined previous researches with the ILs-DBU ^1H NMR spectrum data before and after capturing SO_2 , it is found that the SO_2 reacted with alcoholic hydroxyl firstly in ionic liquids and DBU when SO_2 was absorbed into ILs-DBU and it resulted in new complex sulphur-bearing ionic liquid. Then, the new sulphur-bearing ionic liquid could capture more SO_2 by physical means. The absorbed SO_2 could be released by heating, therefore the absorption system could be recycled. Further application of hydroxyl ammonium ionic liquids-DBU should be enhanced for future large-scale SO_2 scrubbing processes due to its high absorption capacity, good regeneration and low cost.

ACKNOWLEDGEMENTS

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