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Highly efficient sulfur dioxide capture by glyme-lithium salt ionic liquids

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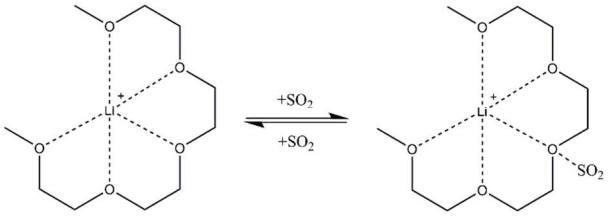
A series of glyme–lithium salt ionic liquids were prepared and applied in SO_2 absorption. The formed quasi-aza-crown ether fashions between Li^+ and glymes can effectively reduce the solvent volatilization, and have an excellent SO_2 absorption capacity. In addition, the mechanism of interaction between SO_2 and ionic liquids was investigated by IR and NMR.

SO_2, mainly emitted from the combustion of fossil fuels, is the main cause of several environmental and human health problems.[1] Thus, the control of SO_2 emission has been a serious problem of global concern. The flue gas desulfurization (FGD) technology widely used over the past decades is limestone scrubbing.[2] However, it still has some inherent drawbacks, including irreversible process, low efficiency, and production of useless byproducts like wastewater and $CaSO_4$. Consequently, new sorbents which can absorb SO_2 efficiently, reversibly, and selectively are still needed.

In recent decades, organic solvents have been used in the research of new sorbents in FGD.[3, 4] In our previous work, solubilities of SO_2 in ethylene glycol derivatives were determined, and the interaction mechanism was also investigated.[5, 6] It indicates that ethylene glycol dimethyl ethers exhibit better SO_2 absorptions than ethylene glycol because of the charge-transfer interaction between S atoms and O atoms. In addition, the solvents can be regenerated by N_2 bubbling and heating. However, volatilization of the solvents occurs in the regeneration process of industrial application, which may cause the VOCs pollution. Ionic liquids (ILs) with unique properties, such as high thermal stability, negligible vapour pressure, wide liquid temperature range, and tunable structure, have been widely investigated in FGD. Numerous ILs based on guanidinium,[7-9] imidazolium,[10-12] pyridinium,[13] and phosphonium[14] have been prepared and applied in SO_2 removal. Furthermore, ether-functionalized[15-21] and anion-functionalized task-specific ionic liquids[22-24] were synthesized to improve the SO_2 absorption capacity, which is attributed to the multiple binding sites for SO_2 in the functionalized ions. Generally, the preparation of ionic liquids needs several steps, and the conventional ILs are far more expensive than organic liquids. So a new kind of ILs, which can be prepared conveniently, is still needed. Hu and co-workers have prepared the acid salt ionic liquids and determined the SO_2 absorption of these ionic liquids. These ionic liquids exhbit good SO_2 absorption ability and low energy consumption.[25, 26]

The interactions between Li^+ and organic solvents, such as crown ethers,[27] poly (ethylene glycol)s,[28] and acetamide,[29] have been widely investigated in the past few years. Because of the coordination effect, lithium salts can dissolve into these solvents, and the obtained mixtures are ionic liquids.[30] These solvents have been widely used in the investigation of supermolecule systems, nonaqueous electrolytes in Li batteries,[31] and CO_2 removal.[32] Here, we prepared a series of glyme-lithium salt ionic liquids, and investigated their absorptions of SO_2.

The glyme-Li salt ionic liquids were simply prepared by stirring and heating at 353 K for 30 min after the mixing of lithium salts and glymes in quantitative yield. The formed products are colourless and transparent ionic liquids. The cations of the ionic liquids are formed by complexation of Li^+ and neutral ligands such as tetraglyme (as shown in scheme 1).[30] Here, different kinds of glymes, including glyme (G1), diglyme (G2), triglyme (G3) and tetraglyme (G4) were selected to prepare the target ionic liquids, and both of urea and tetraethylene glycol were also employed to make a comparison. What's more, different Li salts like $LiNTf_2$, $LiClO_4$, LiOTf, and $LiBF_4$ was also used to investigate the effect of anions.



Scheme 1 Structure of [Li-tetraglyme]$^+$ ion before and after SO_2 absorption.

The structures of the glyme-Li salt ionic liquids were confirmed by IR and ^{1}H-NMR. For ^{1}H-NMR, an external reference (D_2O) method was used to avoid the solvent effect of deuterated reagents. As shown in Fig. 1, the chemical shifts of all hydrogen atoms in triglyme move upfield from 3.77, 3.93, and 4.02 to 3.63, 3.82, and 3.90, respectively, after the formation of [Li-triglyme][NTf_2]. It's because the deshielding effect caused by oxygen atoms is inhibited owing to the interaction between Li^+ and oxygen atoms in glymes. A similar result was also obtained for [Li-tetraglyme][NTf_2] ionic liquid. (see Fig. S1 in ESI†)

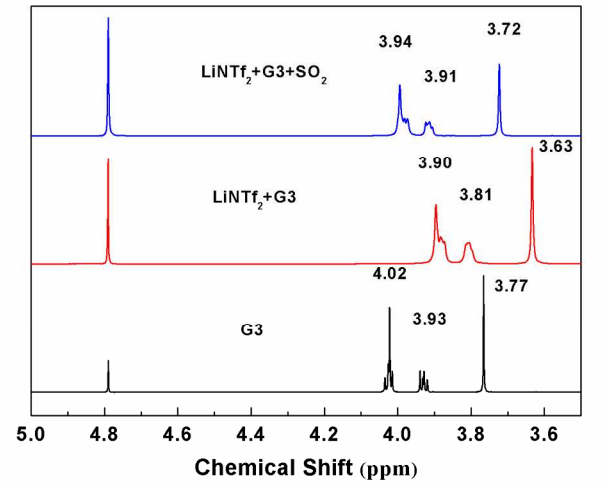


Fig. 1 ^{1}H-NMR spectra of triglyme, [Li-triglyme][NTf_2] and [Li-triglyme][NTf_2] after SO_2 absorption, with D_2O as an external reference.

The thermostability of sorbents used in flue gas desulfurization is also very important. High-boiling solvents can efficiently reduce the volatilization of organic compounds, especially in the regeneration process. Thermal gravimetric analysis (TGA) of the glyme-lithium salt ionic liquids were conducted, and the results are shown in Fig. 2.

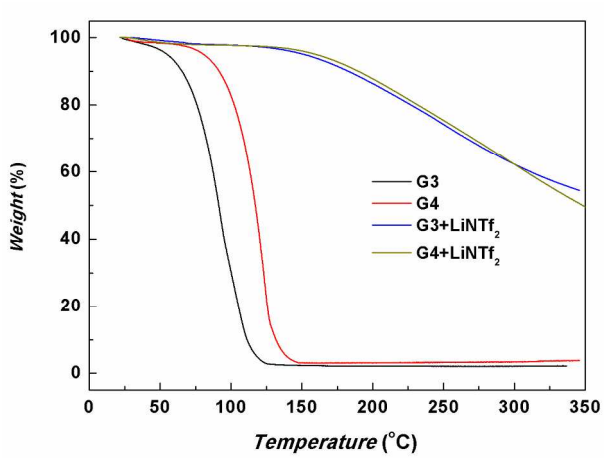


Fig. 2 Thermal gravimetric analysis of triglyme, tetraglyme, [Li-triglyme][NTf_2] and [Li-tetraglyme][NTf_2].

It indicates that the deposition temperature (T_d) of the tetraglyme increases significantly from 379 K to 446 K after the formation of [Li-tetraglyme][NTf_2]. More interestingly, T_d of [Li-triglyme][NTf_2] is almost as high as [Li-tetraglyme][NTf_2], which means the formation of Li-glyme cations can effectively reduce the solution volatilization, especially for small molecules. Considering that the temperature of regeneration process is about 353 K, the [Li-glyme][NTf_2] ionic liquids can be used in SO_2 absorption and deposition cycles without a significant solvent loss.

The SO_2 absorption capacity of each glyme-LiNTf_2 ionic liquids was determined at 293 K under ambient pressure, and the results are shown in Fig. 3. The ionic liquids exhibit excellent SO_2 absorption capacities, and the capacity increases in the order: diglyme < glyme < triglyme < tetraglyme, which is nearly in consistent with number of oxygen atoms in glymes. Ionic liquids with different mole ratios of glyme were also taken into consideration, and the result indicates that the SO_2 absorption capacity increases with the mole ratio of glyme. However, the ionic liquid with a higher ratio of G1 volatilizes obviously at the temperature above 293 K. As in literature,[7,10] SO_2 absorptions of [TMG][L] and [BMIM][BF4] are 1.7 and 1.50, respectively. Compared to the common ionic liquids, the Li salt ionic liquids exhbit an acceptable absorption ability.

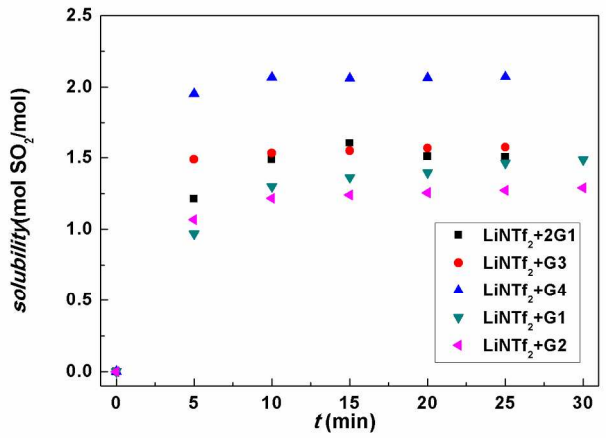


Fig. 3 SO_2 absorption curves of different glyme-$LiNTf_2$ ionic liquids at 293 K.

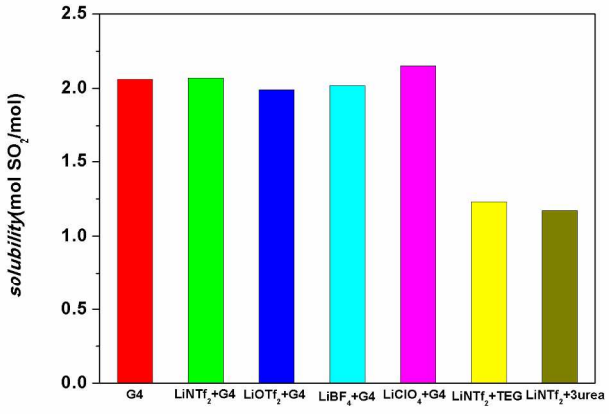


Fig. 4 SO_2 absorption capacities of tetraglyme, [Li-tetraglyme][X], [Li-TEG][NTf_2] and [Li-3urea][NTf_2] ionic liquids at 293 K. (X= NTf_2, OTf, BF_4, and ClO_4)

The influences of temperature and SO_2 partial pressure on SO_2 absorption of glyme-$LiNTf_2$ were investigated. (Fig. S2 and Fig. S3 in ESI†) As temperature increases, the SO_2 absorption capacities of all ionic liquids decrease. Meanwhile, the absorption capacities increase linearly with the SO_2 partial pressure. We also determined the SO_2 absorption of glyme-$LiNTf_2$ with the SO_2 partial pressure of 800 Pa, and the absorption capacity is 0.007 mol SO_2/mol IL, which indicated that the absorption process is physical absorption. The results demonstrate that both heating and N_2 bubbling can be effective ways to regenerate the solvents when applied in SO_2 removal, and vacuum regeneration with heating is also desirable for the SO_2 regeneration. The regeneration experiments were performed with six absorption-desorption cycles, and the ionic liquids can be reused without a significant loss of SO_2 absorption capacity. (Fig. S4 in ESI†)

A comparison of SO_2 absorption capacities between [Li-tetraglyme] salts with different anions were conducted, and the results are shown in Fig. 4. The absorption capacity has no significant changes when the anion of $[NTf_2]^-$ is replaced by $[OTf]^-$, $[BF_4]^-$ or $[ClO_4]^-$, which means the $[Li\text{-glyme}]^+$ cation plays the main role in the absorption process. The SO_2 absorption experiments of tetraglyme, [Li-tetraethylene glycol (TEG)][NTf_2], and [Li-3 urea][NTf_2] also support the conclusion above. The absorption capacities of the three solvents at 293 K are 2.06, 1.23, and 1.17 mol SO_2 per mol ionic liquid, respectively, while the value is 2.07 for [Li-tetraglyme][NTf_2]. The SO_2 absorption capacity is almost the same for tetraglyme before and after interaction with lithium salts. Compared with urea and TEG, tetraglyme exhibits a better SO_2 absorption capacity. However, the viscosity of the formed ionic liquid is extremely high. For tetraglyme, the viscosity is 3.295 mPa·s at 298.15 K as in literature,[33] while the value is 185 mPa·s for [Li-tetraglyme][ClO_4]. The high viscosity may be a limitation of the ionic liquid in the industrial application.

The interaction between glyme-lithium salt ionic liquids and SO_2 was investigated by IR and ^{1}H-NMR. In Fig. 1, we can see that after the absorption of SO_2, all chemical shifts of hydrogen atoms in [Li-triglyme] [NTf_2] move downfield, which is because of the aromatic solvent-induced shift caused by SO_2. As in literature,[6] external reference ^{1}H-NMR of triglyme before and after SO_2 absorption have the similar result. Considering of the absorption result, the mechanism of interaction between ionic liquids and sulfur dioxide are similar to that of glymes based on the charge-transfer interaction between sulfur atoms in SO_2 and oxygen atoms in glymes. As for IR spectra (Fig. S5 in ESI†), no new band appears after the absorption of SO_2, which means the process is physical absorption. It must be noted that the typical vibrational peaks of SO_2 are covered by the vibrational peaks of $[NTf_2]^-$, so the peaks of SO_2 can't be observed significantly in the figure.

In summary, a series of glyme-lithium salt ionic liquids were prepared, and characterizations of their structures were conducted. The formed $[Li\text{-glyme}]^+$ can effectively improve the thermal stability and reduce the volatilization. Absorption capacities of the ionic liquids were determined, and the influences of temperature and SO_2 partial pressure were also taken into consideration. The results demonstrate that the ionic liquids can efficiently absorb SO_2 and have an excellent regeneration property. In addition, ^{1}H-NMR and IR were employed to analyse the absorption mechanism of SO_2 in these ionic liquids, which indicate that charge-transfer interaction between sulfur atoms and oxygen atoms is the main force. Finally, glyme-lithium salt ionic liquids with high thermal stability and excellent SO_2 absorption capacity can be promising alternatives in SO_2 removal.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, SO_2 absorption data, and IR and ^{1}H-NMR spectra for ionic liquids before and after absorption. See DOI: 10.1039/c000000x/

1. J. D. Spengler, B. G. Ferris Jr, D. W. Dockery and F. E. Speizer, *Environ. Sci. Technol.*, 1979, **13**, 1276-1280.
2. V. Kaplan, E. Wachtel and I. Lubomirsky, *Rsc Adv.*, 2013, **3**, 15842-15849.
3. M. H. H. vanDam, A. S. Lamine, D. Roizard, P. Lochon and C. Roizard, *Ind. Eng. Chem. Res.* , 1997, **36**, 4628-4637.
4. R. de Kermadec, F. Lapicque, D. Roizard and C. Roizard, *Ind. Eng. Chem. Res.*, 2002, **41**, 153-163.
5. J. B. Zhang, P. Y. Zhang, G. H. Chen, F. Han and X. H. Wei, *J. Chem. Eng. Data*, 2008, **53**, 1479-1485.
6. S. Sun, Y. Niu, Z. Sun, Q. Xu and X. Wei, *Rsc Adv.*, 2014, **5**, 8706-8712.
7. W. Wu, B. Han, H. Gao, Z. Liu, T. Jiang and J. Huang, *Angew. Chem. Int. Ed.*, 2004, **43**, 2415-2417.
8. G. Yu and X. Chen, *J. Phys. Chem. B*, 2011, **115**, 3466-3477.
9. Y. Wang, C. Wang, L. Zhang and H. Li, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5976-5982.
10. J. Huang, A. Riisager, P. Wasserscheid and R. Fehrmann, *Chem. Commun.*, 2006, 4027-4029.
11. M. B. Shiflett and A. Yokozeki, *Energy Fuels*, 2010, **24**, 1001-1008.
12. A. Yokozeki and M. B. Shiflett, *Energy Fuels*, 2009, **23**, 4701-4708.
13. S. J. Zeng, H. S. Gao, X. C. Zhang, H. F. Dong, X. P. Zhang and S. J. Zhang, *Chem Eng J*, 2014, **251**, 248-256.
14. G. F. Qu, J. Zhang, J. Y. Li and P. Ning, *Sep Sci Technol*, 2013, **48**, 2876-2879.
15. S. Y. Hong, J. Im, J. Palgunadi, S. D. Lee, J. S. Lee, H. S. Kim, M. Cheong and K.-D. Jung, *Energy Environ. Sci.*, 2011, **4**, 1802-1806.
16. Z. Z. Yang, L. N. He, Q. W. Song, K. H. Chen, A. H. Liu and X. M. Liu, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15832-15839.
17. Z. Z. Yang, L. N. He, Y. N. Zhao and B. Yu, *Environ. Sci. Technol.* , 2013, **47**, 1598-1605.
18. L. H. Zhang, Z. J. Zhang, Y. L. Sun, B. Jiang, X. G. Li, X. H. Ge and J. T. Wang, *Ind. Eng. Chem. Res.* , 2013, **52**, 16335-16340.
19. Y. Zhao, J. Y. Wang, H. C. Jiang and Y. Q. Hu, *J. Mol. Liq.*, 2014, **196**, 314-318.
20. G. Cui, C. Wang, J. Zheng, Y. Guo, X. Luo and H. Li, *Chem. Commun.*, 2012, **48**, 2633-2635.
21. S. K. Tang, G. A. Baker and H. Zhao, *Chem. Soc. Rev.*, 2012, **41**, 4030-4066.
22. C. Wang, G. Cui, X. Luo, Y. Xu, H. Li and S. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 11916-11919.
23. G. K. Cui, J. J. Zheng, X. Y. Luo, W. J. Lin, F. Ding, H. R. Li and C. M. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 10620-10624.
24. C. M. Wang, J. J. Zheng, G. K. Cui, X. Y. Luo, Y. Guo and H. R. Li, *Chem. Commun.* , 2013, **49**, 1166-1168.
25. K. Huang, Y. L. Chen, X. M. Zhang, S. Xia, Y. T. Wu and X. B. Hu, *Chem. Eng. J.*, 2014, **237**, 478-486.
26. K. Huang, G. N. Wang, Y. Dai, Y. T. Wu, X. B. Hu and Z. B. Zhang, *Rsc Adv.*, 2013, **3**, 16264-16269.
27. M. M. Meinholz, E. Carl, E. Kriemen and D. Stalke, *Chem. Commun.*, 2011, **47**, 10948-10950.
28. Y. Tominaga and H. Ohno, *Chem. Lett.*, 1998, 955-956.
29. Y. S. Hu, H. Li, X. J. Huang and L. Q. Chen, *Electrochem. Commun.*, 2004, **6**, 28-32.
30. K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko and M. Watanabe, *J. Phys. Chem. B*, 2012, **116**, 11323-11331.
31. Y. Lin, J. Li, Y. Q. Lai, C. F. Yuan, Y. Cheng and J. Liu, *Rsc Adv.*, 2013, **3**, 10722-10730.
32. C. Wang, Y. Guo, X. Zhu, G. Cui, H. Li and S. Dai, *Chem. Commun.*, 2012, **48**, 6526-6528.
33. A. Pal and G. Dass, *J. Mol. Liq.*, 2000, **84**, 327-337.

