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Highly Efficient and Reversible SO_2 Capture by Tunable Azole-Based Ionic Liquids through Multiple-Site Chemical Absorption

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S *Supporting Information*

ABSTRACT: A novel strategy for SO_2 capture through multiple-site absorption in the anion of several azole-based ionic liquids is reported. An extremely high capacity of SO_2 (>3.5 mol/mol) and excellent reversibility (28 recycles) were achieved by tuning the interaction between the basic anion and acidic SO_2. Spectroscopic investigations and quantum-mechanical calculations showed that such high SO_2 capacity originates from the multiple sites of interaction between the anion and SO_2. These tunable azole-based ionic liquids with multiple sites offer significant improvements over commonly used absorbents, indicating the promise for industrial applications in acid gas separation.

Ionic liquids (ILs) have recently attracted considerable attention because of their unique properties, including negligible vapor pressures, wide liquid temperature ranges, high thermal stabilities, and tunable properties.[1] They have been widely used in the field of acid gas separation for gases such as CO_2,[2] SO_2,[3] BF_3,[4] and so on. Generally, the gas absorption by these ILs is mainly based on single-site interactions between the IL and the acid gas. Therefore, it is very important to increase the number of interaction sites between the IL and the acid gas in order to achieve highly efficient gas absorption. Herein we report a novel strategy for the capture of SO_2 by several tunable azole-based basic ILs with multiple sites of action. We show how we can obtain an extremely high capacity (up to 4.8 mol of SO_2/mol of IL) and excellent reversibility by tuning the interaction between the IL anion and SO_2.

The emission of SO_2 in flue gases from the burning of fossil fuels has drawn worldwide attention because it is a significant source of atmospheric pollution that threatens the environment and human health. Accordingly, the development of new materials that can efficiently, reversibly, and economically capture SO_2 is highly sought. Effective capture of SO_2 from flue gas requires strong chemical absorption because of the relatively low partial pressure (e.g., 0.2 vol % SO_2) in the gas.[5] The conventional technologies to remove SO_2, such as limestone scrubbing, ammonia scrubbing, and organic solvent absorption, have some inherent disadvantages, including their byproducts (e.g., calcium sulfate) and the volatilization of solvents.[6] Han and co-workers have reported the first example of SO_2 chemisorption that employs a base-functionalized IL, 1,1,3,3-tetramethyguanidinium lactate ([TMG][lactate]), where ~1.0 mol of SO_2/mol of IL can be absorbed at 1 bar with 8% SO_2 in the gas.[3a] Subsequently, some other basic ILs, including those with acetate and methyl sulfate anions, have been reported for the chemical capture of SO_2.[7] Normally, traditional chemisorption of SO_2 is based on the strong interaction between the electronegative oxygen ions in the anion (e.g., acetate) and SO_2, and thus, up to 1:1 stoichiometry would be achieved at low pressure. In addition, in comparison with physical absorption, chemical absorption often has a high absorption enthalpy, which means that high energy is required for regeneration.[8] We need to increase the number of interaction sites between the IL and SO_2 to improve the absorption capacity as well as reduce the absorption enthalpy to save the energy for regeneration. Thereby, it is highly important to know how to design highly efficient and reversible ILs with multiple sites for the capture of SO_2 by increasing the number of interaction sites for SO_2 in the ILs.

In this work, we describe a new method for the multiple-site capture of SO_2 involving the use of azole-based ILs that were prepared by neutralizing several different azoles with phosphonium hydroxide (see Chart 1 for their structures). We show that an extremely high capacity (up to 4.8 mol of SO_2/mol of IL) for SO_2 capture can be achieved by making use of the reactivity of multiple electronegative nitrogen atoms of the anion in these azole-based ILs. Furthermore, the absorption enthalpy was facilely tuned by the interaction between the anion and SO_2, providing excellent reversibility (28 recycles).

These azole-based ILs were prepared by the acid—base neutralization between tetrazole (Tetz) or imidazole (Im) and a solution of phosphonium hydroxide in ethanol, which was synthesized by the anion-exchange method.[9] The structures of these azole-based ILs were verified by NMR and IR spectroscopy [see the Supporting Information (SI)]. Thermogravimetric analysis showed that the stability of these ILs is high. Especially $[P_{66614}][Tetz]$, whose decomposition temperature is higher than 320 °C, is significantly more stable than normally used strongly basic ILs.[10]

The effect of pressure on the SO_2 absorption by two kinds of typical azole-based ILs $[P_{66614}][Tetz]$ and $[P_{66614}][Im]$ was investigated (Figure 1a). It was seen that the molar ratios of SO_2 to IL for $[P_{66614}][Tetz]$ and $[P_{66614}][Im]$ decreased from 3.72 to 1.54 and 4.80 to 2.07, respectively, as the pressure decreased from 1.0 to 0.1 bar. Clearly, the SO_2 capacity is

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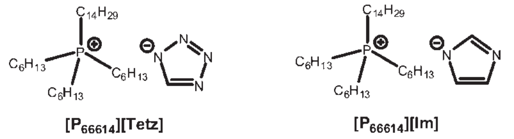
Chart 1. Structures of the Azole-Based Ionic Liquids



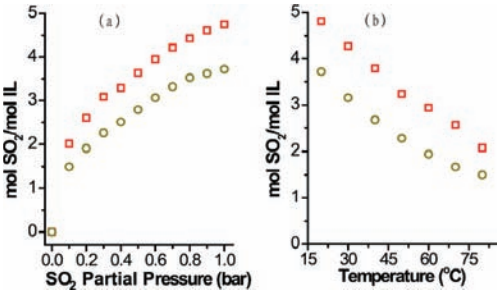


Figure 1. Effect of (a) pressure and (b) temperature on SO_2 absorption by some azole-based ionic liquids: [P_{66614}][Im], red □; [P_{66614}][Tetz], green ○.

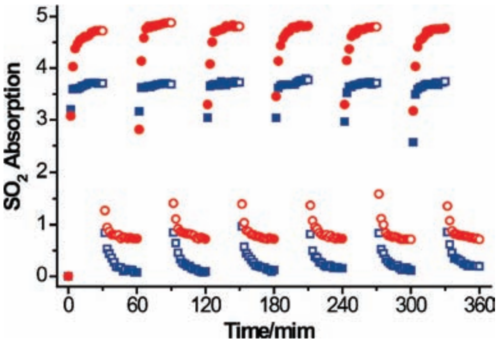


Figure 2. Comparison of the SO_2 absorption/desorption processes for different azole-based ILs. SO_2 absorption was carried out at 20 °C, and desorption was performed at 80 °C under N_2. [P_{66614}][Tetz]: absorption, blue ■; desorption, blue □. For [P_{66614}][Im]: absorption, red ●; desorption, red ○.

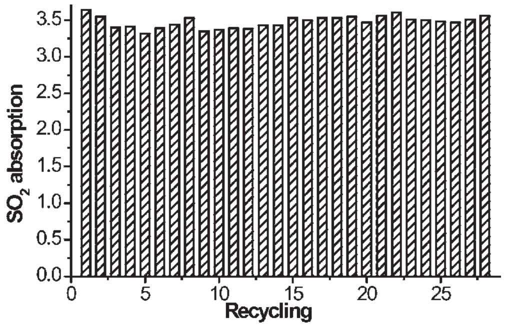


Figure 3. SO_2 absorption by [P_{66614}][Tetz] for 28 cycles. SO_2 absorption was carried out at 20 °C for 30 min, and desorption was performed at 80 °C under N_2 for 30 min.

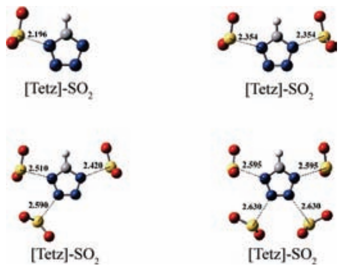


Figure 4. Optimized structures showing multiple-site interactions between the anion [Tetz] and SO_2: (a) [Tetz]−SO_2, $\Delta H = -89.3$ kJ mol^{-1}; (b) [Tetz]−2SO_2, $\Delta H = -59.9$ kJ mol^{-1}; (c) [Tetz]−3SO_2, $\Delta H = -39.7$ kJ mol^{-1}; (d) [Tetz]−4SO_2, $\Delta H = -34.4$ kJ mol^{-1}.

significantly greater than 1:1 stoichiometry, even at low pressure. Figure 1b shows the temperature dependence of the SO_2 absorption at 1 bar. As can be seen in Figure 1b, the absorption capacity decreased significantly as the temperature increased. For example, the SO_2 absorption capacity of [P_{66614}][Tetz] decreased continuously from 3.72 to 1.50 mol of SO_2/mol of IL as the temperature increased from 20 to 80 °C. These results indicate that the captured SO_2 is facilely stripped by heating or bubbling N_2 through the IL. The effect of different flue gas constituents on SO_2 capture was also investigated (Table S2 in the SI). As can be seen, the effect of other flue gas constituents (e.g., water and CO_2) on the capture of SO_2 by [P_{66614}][Tetz] is weak.

Figure 2 compares the SO_2 absorption/desorption processes exhibited by [P_{66614}][Tetz] and [P_{66614}][Im]. As shown, all of the absorption capacities of [P_{66614}][Tetz] remained steady, and the absorption and desorption rates were high. For [P_{66614}][Im], the desorption of SO_2 was not complete: ~0.7 mol of SO_2/mol of IL remained, thus resulting in an absorption capacity of ~4.0 mol of SO_2/mol of IL during the SO_2 absorption. This indicates that the anion in the azole-based ILs is important to the release of SO_2. For comparison, for [TMG][lactate] and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]), the desorption of SO_2 is not easy at 80 °C, and their absorption capacities decrease during the recycling because of the low stabilities of the ILs and their strong interactions with SO_2.[7b,11]

The absorption/desorption recycling of an IL is a critical property for gas absorption that has a direct impact on the cost because it determines the frequency of the IL's replacement.[12] Therefore, we selected [P_{66614}][Tetz] as a sorbent material to investigate the stability of SO_2 absorption during the recycling of the IL. The results for 28 absorption/desorption cycles of [P_{66614}][Tetz] are shown in Figure 3. It is clear that the high absorption capacities and the rapid absorption rates are well-maintained during the 28 cycles, indicating that the SO_2 absorption process by [P_{66614}][Tetz] is highly reversible.

Considering the high absorption capacity of the IL as well as the excellent reversibility, we believe that these azole-based ILs are highly attractive alternatives for SO_2 absorption whose performance is significantly superior to that of traditional ILs and other solid-phase adsorbent materials (Table S1).[13] Why do these azole-based ILs exhibit such high capacities for SO_2 capture? We believe that the electronegative nitrogen atoms in the anion may contribute to multiple-site interactions with SO_2, resulting in high SO_2 absorption capacities for these ILs. Furthermore, we wanted to know the reason why the desorption of SO_2 by these azole-based ILs would be significantly affected by the anion of the ILs.

To investigate the role of the electronegative nitrogen atoms in the anion of IL in SO_2 absorption, theoretical calculations were performed using the Gaussian 03 program. For each set of calculations, we performed geometry and energy optimizations for each free anion, the free SO_2 molecule, and each anion−SO_2 complex at the B3LYP/6-31++G(p,d) level.[14] The optimized structures reflecting the interaction of SO_2 with the anion [Tetz] are shown in Figure 4. We also calculated the energetics of the gas-phase reaction between SO_2 and [Tetz] according to Scheme S1 in the SI. As shown in Figure 4, the calculated absorption enthalpies of SO_2 for the [Tetz]−SO_2, [Tetz]−$2SO_2$, [Tetz]−$3SO_2$, and [Tetz]−$4SO_2$ complexes were −89.3, −59.9, −39.7, and −34.4 kJ mol^{-1}, respectively. During SO_2 absorption by the IL, the interaction between the anion and SO_2 changes gradually from a chemical interaction to a physical interaction because of the decrease in absorption enthalpy.[15] According to the calculated results, the interactions in [Tetz]−SO_2 and [Tetz]−$2SO_2$ are mainly chemical interactions, with absorption enthalpies larger than 50 kJ mol^{-1}. This indicates that an absorption capacity of ∼2 mol of SO_2/mol of IL can be achieved at low pressure, which qualitatively agrees with the experimental results in Figure 1. Furthermore, ∼4 mol of SO_2/mole of IL can be absorbed as a result of multiple-site interactions between the electronegative nitrogen atoms and the sulfur atom with positive charge in the acidic SO_2.

To explain the effect of the anion on the desorption of SO_2, we also calculated the absorption enthalpy of SO_2 by the anion [Im]. The absorption enthalpies for the [Im]−SO_2, [Im]−$2SO_2$, [Im]−$3SO_2$, and [Im]−$4SO_2$ complexes were found to be −124.6, −75.7, −36.9, and −30.3 kJ mol^{-1}, respectively, revealing the significantly stronger interaction with [Im] than with [Tetz]. Therefore, the desorption of SO_2 from [P_{66614}][Im] is more difficult than that from [P_{66614}][Tetz]. The different strengths of the interactions between the anions and SO_2 mainly originates from the difference in the atomic charges of the nitrogen atoms.[15,16] For example, the Mulliken charges on the nitrogen atoms in [Tetz] were −0.350, −0.350, −0.123, and −0.123, while those in [Im] were −0.398 and −0.398.

The interactions of the ILs with SO_2 were further investigated by FT-IR and NMR spectroscopy to support the experimental and theoretical results (Figure 5). In comparison with the IR spectrum of the fresh IL [P_{66614}][Tetz], new absorption bands at 1327 and 935 cm^{-1} attributable to sulfate S═O and S−O stretches, respectively, appeared as a result of the absorption of SO_2 (Figure S2).[17] Similarly, after the absorption of SO_2, the typical peaks of the anion [Tetz] in the ^{1}H NMR spectrum moved downfield from 8.28 to 8.92 ppm, and those in the ^{13}C NMR spectrum moved upfield from 149.4 to 142.9 ppm. Furthermore, the ^{15}N NMR spectra also showed the interaction between the IL and SO_2 during the absorption of SO_2, as the peaks moved from 388.9 and 318.9 ppm to 375.5 and 208.9 ppm, respectively (see the SI). On the basis of previous reports[9b,17] and the observed product, the multiple-site absorption mechanism for [P_{66614}][Tetz] is presented in Scheme S1, indicating that a high capacity of SO_2 can be achieved.

In summary, we have developed a new method for capturing SO_2 using some azole-based ILs with multiple sites. These ILs react with SO_2 to form the liquid sulfate salt via the interaction between multiple electronegative nitrogen atoms in the anion and the sulfur atom with positive charge in the acidic SO_2. Thus, an extremely high SO_2 capacity of >3.5 mol/mol of IL was achieved. To the best of our knowledge, these ILs show the highest capacity for SO_2 chemical absorption reported to date. Furthermore, the captured SO_2 was easy to release by heating or bubbling N_2 through the IL to tune the interaction between the anion and SO_2. This method based on using interactions with multiple sites in the anion of azole-based ILs opens a door to achieving high capacity as well as reversibility in the capture of gases such as SO_2, H_2S, and CO_2 by ILs. We believe that this highly efficient and excellently reversible process involving these ILs with multiple sites can provide a potential alternative for SO_2 capture.

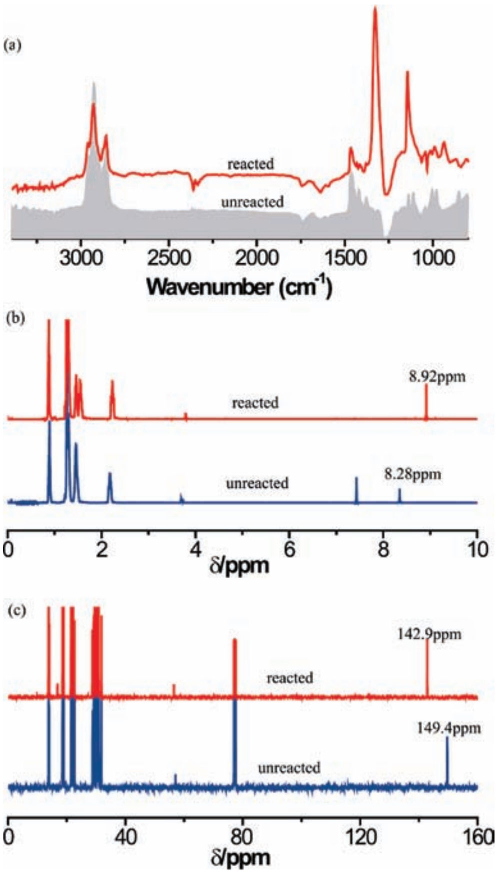


Figure 5. FT-IR, ^{1}H NMR, and ^{13}C NMR spectra of [P_{66614}][Tetz] before and after the reaction with SO_2. (a) FT-IR spectra: [P_{66614}][Tetz]−SO_2 complex (red), [P_{66614}][Tetz] (gray). (b) ^{1}H NMR spectra: [P_{66614}][Tetz]−SO_2 complex (red), [P_{66614}][Tetz] (blue). (c) ^{13}C NMR spectra: [P_{66614}][Tetz]−SO_2 complex (red), [P_{66614}][Tetz] (blue).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental and computational sections, Tables S1 and S2, Figures S1 and S2, and Scheme S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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