Gas Separation

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Tuning Anion-Functionalized Ionic Liquids for Improved SO_2 Capture**

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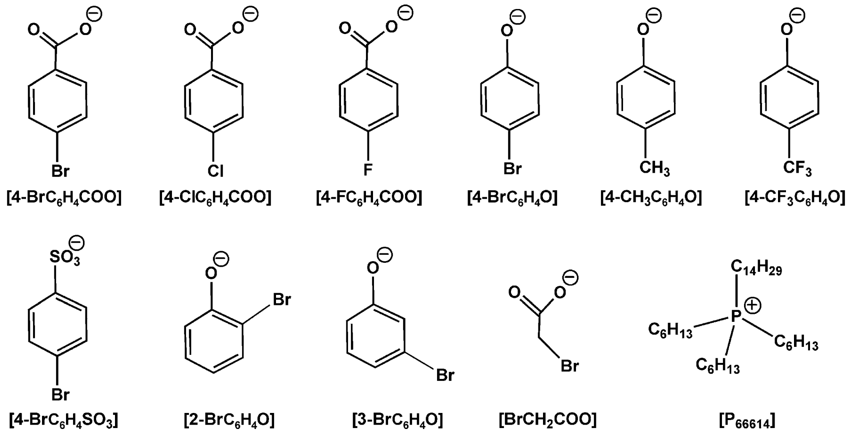
The increase in the concentration of gases such as SO_2 and CO_2 in the atmosphere, which comes from the burning of fossil fuels, threatens environment and human health. Accordingly, the development of new materials and processes for the efficient, reversible, and economical capture of these gases is highly desired and of critical importance. The unique properties of ionic liquids (ILs),[1] including extremely low vapor pressures, wide liquid ranges, high stabilities, and tunable properties, offer an opportunity to address this challenge. Herein, we report a "dual-tuning" approach for improving SO_2 capture by several anion-functionalized ILs. We show that both enhanced capacity and reduced enthalpy can be achieved by introducing an electron-withdrawing interaction site, such as halogen group, onto the anion.

Gases such as SO_2, CO_2, BF_3, and H_2S are expected to have a high solubility in ILs, especially in functionalized ILs.[2] Davis and co-workers reported the first example for the chemical absorption of CO_2 that employs an amino-functionalized IL.[3] Subsequently, a great deal of anion-functionalized ILs, including those based on amino acids,[4] acetates,[5] azoles,[6] and phenolates,[7] have been used to capture these acid gases. Normally, the chemisorption has a high capacity for gas absorption along with a high absorption enthalpy, which results in difficult desorption, as well as high energy demand for regeneration.[8] Several methods, including reducing the basicity[9] and introducing an electron-withdrawing substituent on the anion,[10,6a,7b] have been developed for reducing the absorption enthalpy. However, these methods often lead to reduced capacity, owing to a decrease in the interaction between the IL and the acid gas. The question remains whether both increasing the capacity for efficient absorption and reducing the enthalpy for easy desorption by the tuning of specific structures in an anion-functionalized IL can be achieved.

Herein, we describe a dual-tuning approach for improving SO_2 capture by anion-functionalized ILs. The essence of our strategy for increasing the capacity and reducing the enthalpy is introducing an electron-withdrawing interaction site on the anion. Thus, we designed and prepared several anion-functionalized ILs, including ones based on benzoates, acetates, and phenolates with a halogen group on the anion (Scheme 1). Through a combination of absorption experiments, quantum chemical calculations, and spectroscopic investigation, we show that both enhanced capacity and reduced enthalpy for the capture of SO_2 can be achieved based on the dual role of the halogen group as both an added interaction site and an electron-withdrawing group, which produces an IL with a highly efficient and excellent reversible process for SO_2 capture.



Scheme 1. Structures of the cation and the anion in halogen-containing anion-functionalized ionic liquids for SO_2 capture.

These anion-functionalized ILs containing halogen groups were easily prepared by acid–base neutralization between substituted benzoic acids, substituted acetic acids, or substituted phenols and a solution of phosphonium hydroxide in ethanol, which was obtained by an anion-exchange method.[11] The structures of these halogen-containing ILs were verified by NMR and IR spectroscopy (see the Supporting Information). The physical properties, including the density and viscosity, of these ILs were determined (Supporting Information, Table S1). In general, halogen-containing ILs had higher

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Table 1: The effect of different halogen-containing ionic liquids on SO_2 absorption capacities, interaction enthalpies, and the Mulliken atomic charges of oxygen and halogen atoms.

Anions	Absorption capacities[a]	$\Delta H^{[b,c]}$ [kJ mol^{-1}]	Mulliken charges[c] O	X
[PhCOO]	3.74	–	−0.624	–
[4-BrC_6H_4COO]	4.12	−26.6	−0.620	−0.021
[4-ClC_6H_4COO]	3.93	−16.3	−0.618	0.132
[4-FC_6H_4COO]	3.96	−16.8	−0.625	−0.367
[CH_3COO]	3.48	–	−0.627	–
[$BrCH_2COO$]	3.89	−35.9	−0.583	−0.237
[PhO]	3.02	–	−0.687	–
[4-BrC_6H_4O]	3.22	−50.5	−0.681	−0.096
[2-BrC_6H_4O]	3.35	−51.0	−0.628	−0.104
[3-BrC_6H_4O]	3.17	−40.3	−0.668	−0.087
[4-$CF_3C_6H_4O$]	3.25	−24.7	−0.658	−0.329
[4-$CH_3C_6H_4O$]	3.10	–	−0.693	–
[$PhSO_3$]	3.31	–	−0.638	–
[4-$BrC_6H_4SO_3$]	3.15	−20.6	−0.626	0.003

[a] SO_2 (1 bar) was absorbed at 20 °C for 30 min; values given in units of: mol_{SO_2} per mol_{IL}. [b] Interaction enthalpies of the complexes with a halogen group on the anion with the closest SO_2 molecule. [c] Carried out at the B3LYP/6-31++G(d,p) level of theory.

densities and viscosities than the corresponding non-halogenated analogues.

The effect of different ILs with halogen groups on the absorption of SO_2 was investigated, and is shown in Table 1. It was found that the SO_2 absorption capacities of [P_{66614}][4-BrC_6H_4COO], [P_{66614}][4-ClC_6H_4COO], and [P_{66614}][4-FC_6H_4COO] are 4.12, 3.93, and 3.96 mol_{SO_2} per mol_{IL}, respectively, whereas that of [P_{66614}][PhCOO] is 3.74 mol_{SO_2} per mol_{IL}. It can be seen that, compared to non-halogen-containing benzoate-based ILs such as [P_{66614}][PhCOO], benzoate-based ILs with a halogen group, such as [P_{66614}][4-BrC_6H_4COO], exhibited higher SO_2 absorption capacities. Similarly, the acetate-based ILs and phenolate-based ILs that include bromine groups, [P_{66614}][$BrCH_2COO$] and [P_{66614}][4-BrC_6H_4O], also exhibited enhanced absorption of SO_2 in comparison with that of [P_{66614}][CH_3COO] and [P_{66614}][PhO]. The effect of the position of the halogen group in the phenolate anion on the capture of SO_2 was investigated, and is also shown in Table 1. As can be seen, the capacity varied in the range of 3.17–3.32 mol_{SO_2} per mol_{IL} as the position of the Br group on the phenolate anion changed. Furthermore, the capture of SO_2 by [4-$CH_3C_6H_4O$], which contains an electron-donating group, was also investigated (Table 1). It was seen that the capacity increased somewhat owing to the presence of the electron-donating CH_3 group, which is in agreement with the results by phenolate ILs for CO_2 capture.[7b]

Figure S1 shows the effect of pressure and temperature on SO_2 absorption by [P_{66614}][4-BrC_6H_4COO] and [P_{66614}][PhCOO]. It was seen that the molar ratios of SO_2 to IL for [P_{66614}][4-BrC_6H_4COO] and [P_{66614}][PhCOO] decreased from 4.12 and 3.74 to 1.66 and 1.60, respectively, as the SO_2 partial pressure decreased from 1.0 bar to 0.1 bar (Figure S1 a). The temperature dependence of SO_2 absorption by [P_{66614}][4-BrC_6H_4COO] and [P_{66614}][PhCOO] at 1 bar is shown in Figure S1 b. SO_2 absorption capacities by [P_{66614}][4-BrC_6H_4COO] and [P_{66614}][PhCOO] decreased from 4.12 and 3.74 to 1.60 and 1.48 mol_{SO_2} per mol_{IL}, respectively, when the temperature increased from 20 to 120 °C.

The desorption of SO2 by these halogen-containing ILs was investigated, and is shown in Figure 1 (see also Figure S2). As can be seen, the release of SO_2 by halogen-containing ILs such as [P_{66614}][4-BrC_6H_4COO] at 120 °C is complete, whereas the residual capacity for SO_2 desorption by [P_{66614}][PhCOO] is about 0.35 mol_{SO_2} per mol_{IL}, thus indicating that the desorption of SO_2 improved considerably owing to the presence of the electron-withdrawing bromine group. These halo-containing ILs were compared with other anion-functionalized ILs (Table S2). It was seen that the halogen-containing IL [P_{66614}][4-BrC_6H_4COO] exhibited the highest available capacity of SO_2 absorption (up to 4.12 mole per mol_{IL}) owing to its high absorption and facile desorption. Multiple SO_2 absorption/desorption cycles were investigated for [P_{66614}][4-BrC_6H_4COO] (Figure S3). It can be seen that [P_{66614}][4-BrC_6H_4COO] could be recycled more than six times without a loss of absorption capability, indicating that the process of SO_2 absorption by these halogen-containing functionalized ILs is highly reversible.

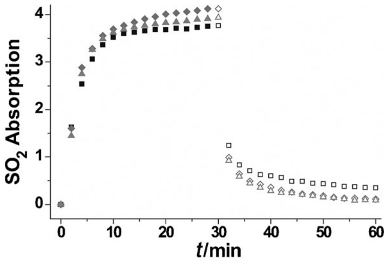

Figure 1. Effect of the halogen group in benzoate-based ionic liquids on SO_2 absorption and desorption as a function of time. SO_2 absorption was carried out at 20 °C, and desorption was performed at 120 °C under N_2. [P_{66614}][4-BrC_6H_4COO]: absorption (◆), desorption (◇); [P_{66614}][4-ClC_6H_4COO]: absorption (▲), desorption (△); [P_{66614}][PhCOO]: absorption (■), desorption (□).

Considering both enhanced absorption and easy desorption by these ILs, halogen groups on the anion play a dual-tuning role for improving the capture of SO_2. Generally, an electron-withdrawing substituent on the anion would reduce the interaction between the anion and acid gas, resulting in decreased capacity. Why do these halogen-containing anion-functionalized ILs exhibit such a different behavior for SO_2 capture? We believe that the different behavior of halogen groups in these ILs may be contributed to by the following two factors: 1) Halogen–sulfur interaction between the halogen group on the anion and SO_2, which leads to an increase in the absorption capacity. 2) The halogen group is an electron-withdrawing group, which disperses the negative charge of the O atoms on the anion and decreases the enthalpy for SO_2 absorption, resulting in the improved desorption. Therefore, the halogen group should play a dual role, both as an added interaction site and as an electron-withdrawing group, which improves the capture of SO_2 considerably.

To investigate the dual role of the halogen group on the anion in these halogen-containing anion-functionalized ILs, we calculated the Mulliken atomic charge of the oxygen and halogen atoms in the anion using the Gaussian 03 program. As can be seen in Table 1, compared with the non-halogen counterpart, the Mulliken atomic charge of the oxygen atom in the halogen-containing anion decreased because of its electron-withdrawing nature, resulting in reduced interaction. For example, the Mulliken atomic charge of the oxygen atom in [4-BrC_6H_4COO] is -0.620, whereas that in [PhCOO] is -0.624. On the other hand, the halogen group shares the negative charge of the oxygen atom in the anion, which enhances halogen–sulfur interaction between the halogen group and SO_2,[12] leading to an increase in the absorption capacity. For example, the Mulliken atomic charge of the Br atom in [4-BrC_6H_4COO] is -0.021, whereas that in bromobenzene is 0.041.

To further investigate the dual role of the halogen group in the capture of SO_2, we calculated the geometry optimization for the free halogen-containing anions, the free SO_2, and the complex of the halogen with the closest SO_2 at the B3LYP/6-31++G(d,p) level of theory.[13] The optimized structures and the energetics, which reflect the interaction between halogen group and SO_2, are shown in Figure 2a (see also Table S3). It can be seen that the intermolecular C(sp^2)−Br⋯S distance in [4-BrC_6H_4COO]–SO_2 is predicted to be 3.267 Å, which corresponds to a reduction of approximately 10.5 % of the sum of the van der Waals radii of the two interacting atoms,[14] whereas the calculated C(sp^2)−Br⋯S angle amounts to 88.2°. The absorption enthalpy for C(sp^2)−Br⋯S interaction of the [4-BrC_6H_4COO]–SO_2 complex was found to be $-26.6\ \mathrm{kJ\,mol^{-1}}$, which indicates that the halogen–sulfur interaction between [4-BrC_6H_4COO] and SO_2 is strong, and results in an increase in the absorption capacity (Table 1). Furthermore, the interaction between the O atoms and SO_2 was also investigated (Figure 2b–d; see also Table S4). It can be seen that the absorption capacities decreased from $-96.9\ \mathrm{kJ\,mol^{-1}}$ and $-55.5\ \mathrm{kJ\,mol^{-1}}$ to $-92.2\ \mathrm{kJ\,mol^{-1}}$ and $-53.7\ \mathrm{kJ\,mol^{-1}}$, respectively, when the bromine group is present on the anion, thus leading to easy desorption. For comparison, the interaction between the halogen group in a halogen-containing anion such as [4-BrC_6H_4O] and CO_2 was also investigated (Figure S4). The interaction in [4-BrC_6H_4O]–CO_2 and [4-BrC_6H_4COO]–CO_2 were lower than that in [4-BrC_6H_4O]–SO_2 and [4-BrC_6H_4COO]–SO_2, thus leading to reduced capacity for CO_2 capture by the halogen-containing anion.[7b]

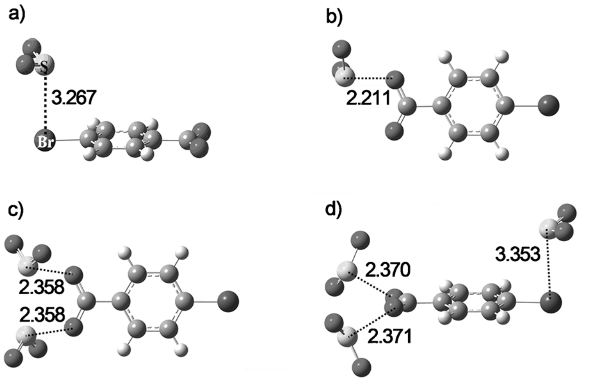

Figure 2. Optimized structures of [4-BrC_6H_4COO]–SO_2 complexes at the B3LYP/6-31++G(d,p) level of theory. a) The Br atom in a [4-BrC_6H_4COO] anion with the closest SO_2 molecule, $\Delta H = -26.6\ \mathrm{kJ\,mol^{-1}}$. b–d) Multiple-site interactions between a [4-BrC_6H_4COO] anion and a SO_2 molecule: b) [4-BrC_6H_4COO]–SO_2, $\Delta H = -92.2\ \mathrm{kJ\,mol^{-1}}$; c) [4-$BrC_6H_4COO$]–2 SO_2, $\Delta H = -53.7\ \mathrm{kJ\,mol^{-1}}$; d) [4-$BrC_6H_4COO$]–3 SO_2, $\Delta H = -19.6\ \mathrm{kJ\,mol^{-1}}$.

The interaction between halogen-containing ILs and SO_2 was further investigated by FTIR and NMR spectroscopy to support the experimental and theoretical results (Figure 3). As can be seen, compared with neat SO_2 at $1150\ \mathrm{cm^{-1}}$ in the FTIR spectra,[15] [P_{66614}][4-BrC_6H_4COO]–SO_2 adducts exhibit a red shift of the symmetric S−O stretching mode, indicating the presence of a halogen–sulfur interaction between the anion and SO_2.[16] Furthermore, compared with the IR spectrum of fresh IL [P_{66614}][4-BrC_6H_4COO], new absorption bands at 1326 and $938\ \mathrm{cm^{-1}}$, which are attributable to the sulfate S−O stretch, are produced[6a] as a result of the absorption of SO_2. Similarly, compared with the fresh IL [P_{66614}][4-BrC_6H_4COO] in the ^{13}C NMR spectrum, the peak of carbon bonded to bromine in the anion moved downfield from 121.9 ppm to 126.3 ppm, as a result of the interaction between the anion and SO_2. Based on previous reports[6a,b] and the observed product, the mechanism of SO_2 absorption by [P_{66614}][4-BrC_6H_4COO] can be proposed as in Figure 2, which posits two kinds of interaction sites between the

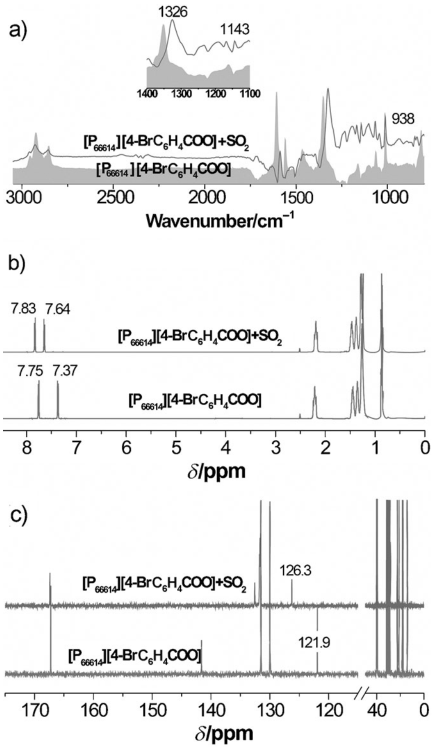

Figure 3. The FTIR (a) ^1H NMR (b) and ^{13}C NMR (c) spectra of [P_{66614}][4-BrC_6H_4COO] before and after the absorption of SO_2.

electronegative oxygen atoms and the halogen atom in the anion with SO_2.

In summary, a new method for SO_2 capture through the addition of an interaction site on the anion to both enhance the absorption capacity and decrease the absorption enthalpy has been developed. Several halogen-containing anion-functionalized ILs exhibited both enhanced capacity and easier desorption than non-halogen-containing ILs, resulting in highly efficient and excellent reversible SO_2 capture. Spectroscopic investigation and quantum-mechanical calculations show that the capacity was increased because of the presence of a halogen–sulfur interaction between the halogen group and SO_2, whereas the desorption properties were improved due to the role of the halogen as an electron-withdrawing group. Aside from these halogen groups, some other electron-withdrawing groups, such as nitrile or aldehyde groups, could also play a dual-tuning role in the capture of gas. The approach developed in this work provides new insight into gas capture, which opens the door to achieving high capacity as well as excellent reversibility, and to capture other gases such as H_2S and CO_2 with ILs. Considering its diversity and tunability, we believe that this highly efficient and reversible process is promising in the field of gas separation.

Experimental Section

Trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}][Cl]$), 4-bromobenzoic acid ($4\text{-}BrC_6H_4COOH$), 4-chlorobenzoic acid ($4\text{-}ClC_6H_4COOH$), 4-fluorobenzoic acid ($4\text{-}FC_6H_4COOH$), benzoic acid (C_6H_5COOH), acetic acid, bromoacetic acid, 4-bromophenol (4-Br-PhOH), 3-bromophenol ($3\text{-}BrC_6H_4OH$), 2-bromophenol ($2\text{-}BrC_6H_4OH$), 4-methylphenol ($4\text{-}CH_3C_6H_4OH$), 4-trifluoromethylphenol ($4\text{-}CF_3C_6H_4OH$), phenol (PhOH), benzenesulfonic acid ($PhSO_3H$) and 4-bromobenzenesulfonic acid ($4\text{-}BrC_6H_4SO_3H$) were all purchased from Sigma–Aldrich. All chemicals were obtained in the highest purity grade possible, and were used as received unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (500 MHz) in $[D_6]$DMSO with tetramethylsilane as the standard. FTIR spectra were recorded on a Nicolet 470 FTIR spectrometer, and in-site IR spectra were recorded on a Bruker MATRIX-MF, respectively. Viscosity was determined by a Brookfield DV II pro viscometer at 25 °C. Decomposition temperatures were measured with a TGA 2100 series of TA Instrument with a heating rate of $10\,°C\,min^{-1}$.

Preparation of ILs: In a typical synthesis of $[P_{66614}][4\text{-}BrC_6H_4COO]$, an equimolar amount of $4\text{-}BrC_6H_4COOH$ was added to an ethanol solution of $[P_{66614}][OH]$, which was prepared from $[P_{66614}][Cl]$ by anion-exchange. The mixture was then stirred at RT for 24 h. Subsequently, ethanol and water were distilled off at 60 °C under reduced pressure. The ILs obtained were dried under high vacuum for 24 h at 60 °C to reduce possible traces of water. The structures of these ILs were confirmed by NMR and IR spectroscopy; no impurities were found by NMR. The water content of these ILs was determined with a Karl Fisher titration and found to be less than 0.1 wt %. The residual chloride content of these ILs was determined by a semiquantitative Nessler cylinder method, which showed that the bromine content was lower than 0.15 wt %.

Absorption and desorption of SO_2: In a typical SO_2 absorption experiment, atmospheric pressure SO_2 was bubbled through IL (ca. 1.0 g) in a glass container with an inner diameter of 10 mm, with a flow rate of about $60\,mL\,min^{-1}$ under 20 °C. The glass container was partly immersed in a circulation water bath of desired temperature. The amount of SO_2 absorbed was determined at regular intervals by an electronic balance with an accuracy of ±0.1 mg.[6,9] The standard deviation of the absorption loadings under 1.0 bar is 0.05 mol_{SO_2} per mol_{IL}. The ILs were regenerated by heating or bubbling through with nitrogen. In a typical SO_2 desorption experiment, atmospheric pressure N_2 was bubbled through about 1.0 g captured ILs in a glass container, which was partly immersed in a circulation oil bath of desired temperature, with a flow rate of about $60\,mL\,min^{-1}$ at 120 °C. The release of SO_2 was determined at regular intervals by electronic balance.

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