Effects of Halide Anions to Absorb SO₂ in Ionic Liquids

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Ionic liquids with halide anions were prepared and the dependency of halide anions on the SO₂ solubility of ILs was investigated. The study shows that the SO₂ solubility of ionic liquids lies in the range 1.91 ~ 2.22 SO₂/ILs mol ratio. SO₂ solubility in ionic liquids with varying halide anions follows the order Br > Cl > I. Theoretical investigation was also conducted at the B3LYP level using the Gaussian 03 program. From the theoretical consideration of the interaction between SO₂ and [EMIm]X (where X = Cl, Br, and I), it has been proposed that primary interaction of halide occurs with C₂-H of the imidazolium and S of SO₂. Experimental results further shows that the absorption and desorption process of SO₂ in ILs was reversible by the three cycles of the absorption at 50 °C and desorption at 140 °C. The reversibility of SO₂ absorption was confirmed by FT-IR studies.

Key Words: Ionic liquids, SO₂ absorption, SO₂ solubility, Anionic effect

Introduction

The absorption processes have been used to remove and recover SO₂ in flue gases from the combustion of sulfur-containing fossil fuels.[1] The conventional SO₂ removal processes such as lime and magnesia scrubbing result in lots of waste water, which is not consistent with the sustainable principles. The solvent absorption processes can be a promising technology by minimizing the additional pollutants by simple recovery of SO₂ by pressure swing or temperature swing. The selection of a good solvent is of critical importance for the SO₂ recovery in the absorption process.[2]

SO₂ absorption processes can also be applied to the SO₂ recovery in SO₂-O₂ stream from a sulfuric acid decomposition unit in a SI (sulfur-iodine) cycle to produce hydrogen using VHTR (very high temperature reactor). Especially, the volatile organic solvents are not proper for the SO₂ recovery in the SI cycle because the SI cycle is a closed-loop process.[3]

Ionic liquids (ILs) have been considered as the absorbents of SO₂, owing to their unique properties such as low volatility, non-flammability and chemical stability.[4-5] Especially, the nonvolatility of ILs makes them good absorbents to separate SO₂ in the SO₂-O₂ stream from the sulfuric acid decomposition in the SI cycle as well as to remove SO₂ from flue gases.[6-8]

It has already been reported that SO₂ could be absorbed in [1,1,3,3-tetramethylguanidine][lactate] through both physical and chemical interactions,[9] while it was demonstrated by IR and NMR analyses that SO₂ was reversibly absorbed in [1,1,3,3-tetramethylguanidine][BF₄] through physical absorption.[10] It was proposed that the cations of ILs were mostly responsible for the SO₂ absorption. Later, the investigation of the anion and cation effects on SO₂ absorption of ILs in a SO₂-O₂ stream by our group demonstrated that the SO₂ solubility in ILs was mostly dependent on the anions in ILs.[3] The SO₂ solubility investigation in ILs from first-principle calculation also suggested that the IL anion-gas interaction play a key role in deciding the gas solubility

in ILs, particularly for polar gases such as SO₂.[11]

In this report, ILs with halide anions were prepared and the dependency of halide anions on the SO₂ solubility of ILs was investigated. High solubility of IL with Cl anion in our earlier reported work[3] prompted us to investigate further the role of anions in IL-SO₂ absorption system. The interaction energy between SO₂ and ILs with halide ions was calculated and correlated with the experimental SO₂ solubility.

Experimental

Halide anion effects of ILs were investigated using eight IL samples: [BMIm]Cl (1-butyl-3-methylimidazolium chloride; Aldrich 97%), [BMIm]Br (Aldrich, 97%), [BMIm]I (prepared), [EMIm]Cl (1-ethyl-3-methylimidazolium chloride; c-tri Korea, 98%), [HMIm]Cl (1-hexyl-3-methylimidazolium chloride; c-tri Korea, 98%), [OMIm]Cl (1-octyl-3-methylimidazolium chloride; c-tri Korea, 98%), [BMpyri]Cl (1-butyl-4-methylpyridinium chloride; prepared, 98%) and [BMpyrr]Cl (1-butyl-4-methylpyrrolidinium chloride; prepared, 98%).

For the preparation of [BMIm]I, [BMIm]Cl (0.05 mol) was dissolved in acetonitrile. NaI (0.05 mol) was added in the [BMIm]Cl solution, which was stirred at room temperature for 48 h. Then, the solution was filtered to remove KCl, and dried with MgSO₄. After evaporating acetonitrile, the resulting sample was dried in a vacuum evaporator. The yield of [BMIm]I was about 90%.

For the preparation of [BMpyrr]Cl, 1-methylpyrrolidine (0.05 mol) was dissolved in toluene. Chlorobutane was added in the 1-methylpyrrolidine solution, which was stirred at room temperature for 10 h. After the purification, the resulting sample was dried in a vacuum evaporator. The yield of [BMpyrr]Cl was about 83%. [BMpyri]Cl was prepared following the same procedure as [BMpyrr]Cl.

The absorption and desorption measurements were conducted by the following experimental apparatus and procedures. An

accurate quantity of ionic liquids was loaded in the glass tube which was set on an analytical balance, and its temperature was controlled by an electric heater. Then, SO_2 gas was introduced into the glass tube containing the ionic liquid at a constant flow rate (20 cc/min) and the weight changes were monitored by means of the analytical balance (Ohaus explore-4200) with an accuracy of ± 0.01 g. It was confirmed that there was no weight variation in the blank test tube experiments where SO_2 gas was allowed to flow at the same rate.

The absorption spectra of ILs before and after gas flow were measured by an IR spectroscopy (Perkin-Elmer 2000). The absorption spectra of SO_2-absorbed ionic liquids were therefore compared with those of pure ionic liquids.

The thermal stability of the ILs was examined by TGA (Thermo Gravimetric Analysis). The decomposition temperature (T_d) was expressed as the temperature at which the 5% weight loss of the initial ILs was observed by TGA. The meaning of T_d can be best described as the starting temperature of the ILs decomposition stage.

The interactions between [EMIm]X (where X = Cl, Br, and I) and SO_2 were theoretically investigated using a Gaussian 03 program.[12] The geometry optimizations and thermodynamic corrections without including the bulk solvent effect were performed with hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31 + G* basis sets for C, H, N and O, and LanL2DZ(ECP) basis sets for S, Cl, Br and I. In order to obtain the most stable geometries, all kinds of possible interaction patterns were optimized. No restrictions on symmetries were imposed on the initial structures. All stationary points were verified as minima by full calculation of the Hessian and a harmonic frequency analysis.

Results and Discussion

Table 1 shows T_d of the tested ILs from TGA experiments. The weight of ILs decreased at about 100 °C during TGA, which can be due to the absorbed water loss in ILs. Especially, [BMIm]Cl, [HMIm]Cl, [OMIm]Cl and [BMpyrr]Cl showed high weight loss at about 100 °C, indicating that those ILs absorbed much water. Therefore, T_d values of those ILs were determined as des-

cribed in experiments after neglecting the weight loss by the pre-absorbed water in the ILs. The T_d values of the ILs are not so much different. It can be said that the ILs are stable at the temperature lower than 200 °C.

Table 1 also shows SO_2 solubility of the IL samples at 50 °C. The solubility data were taken after the weight remained unchanged for 20 min. [BMIm]Cl and [EMIm]Cl showed similar solubility in terms of the mole ratio. [HMIm]Cl showed the solubility slightly higher than [BMIm] and [EMIm] because of a more free volume within the molecular packing as similarly found in the imidazolium-based homologs. It should be noted that [HMIm]Cl, [OMIm]Cl, [BMPyri]Cl and [BMPyrr]Cl had similar solubility curves, confirming that the cationic effects on the SO_2 solubility were not so important. It can also be said that halide effect on the SO_2 solubility is not so important, although the solubility differences were clear in the order of Br > Cl > I (The errors in the solubility were within ± 0.02) which cannot be explained by difference in free volume.

Figure 1 shows the absorption and desorption behaviors of SO_2 in [BMIm]Cl. Three cycles were done without the loss of the SO_2 absorption capability. The SO_2 absorption was conducted at 50 °C and atmospheric pressure (P_{SO_2} = 1 atm). The solubility of SO_2 in [BMIm]Cl was 2.06 SO_2-mol/ILs-mol. The desorption rate was so slow that the total desorption could be achieved by purging with N_2 (20 mL/min) at 140 °C, indicating
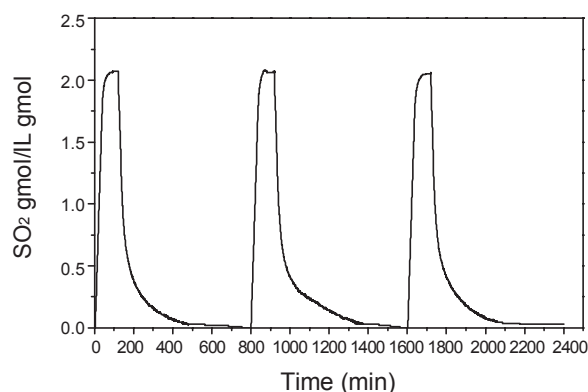

Figure 1. SO_2 absorption and desorption cycles in [BMIm]Cl; SO_2 absorption in SO_2 stream of 20 mL/min at 50 °C and SO_2 desorption in N_2 stream of 10 mL/min at 140 °C

Table 1. Thermal stability and SO_2 solubility of ionic liquids by TGA analysis

Ionic Liquids	$T_d/°C^a$	SO_2 solubility^b SO_2/ILs (mol/mol)
[BMIm]Cl	237	2.06
[BMIm]Br	252	2.11
[BMIm]I	240	1.91
[EMIm]Cl	233	2.03
[HMIm]Cl	225	2.19
[OMIm]Cl	224	2.19
[BMPyri]Cl	218	2.22
[BMPyrr]Cl	213	2.22

$^a T_d$ is the temperature at which decomposition begins and corresponds to the 5% weight loss calculated from dynamic TGA in air. $^b SO_2$ solubility was measured at 50 °C and atmospheric pressure
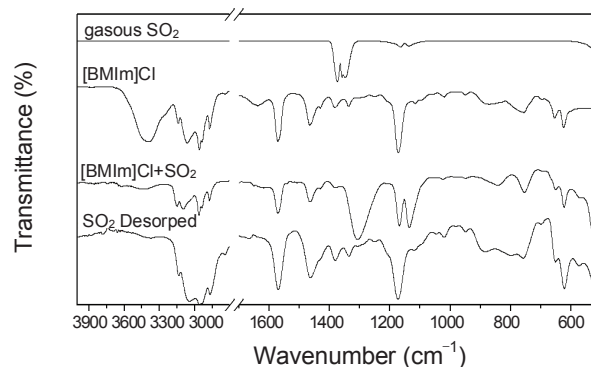

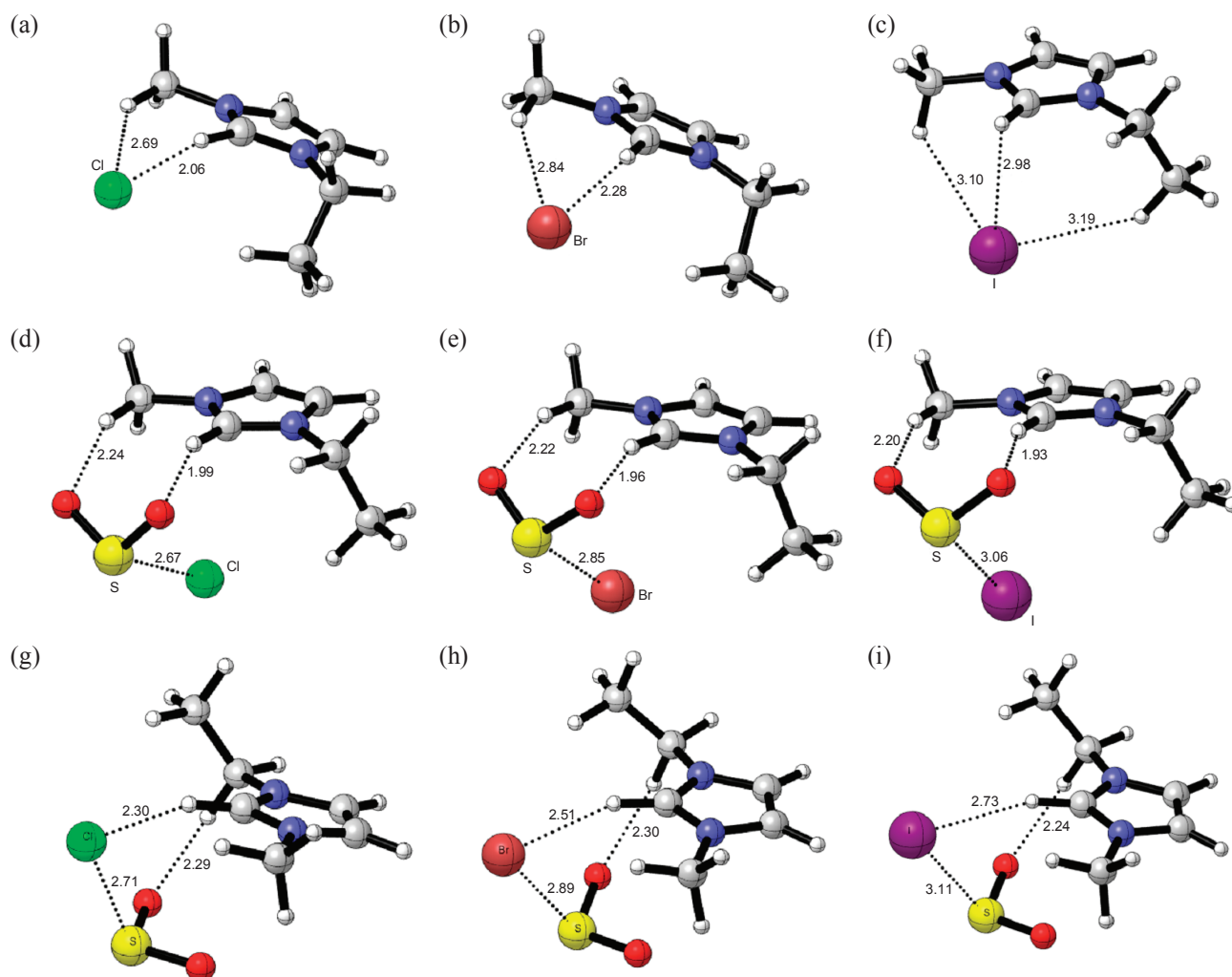**Figure 2.** FT-IR spectra of SO_2 gas, pure [BMIm]Cl, SO_2-[BMIm]Cl, and SO_2 desorbed [BMIm]Cl.

Figure 3. Optimized structures showing (a) [EMIM]Cl, (b) [EMIM]Br, (c) [EMIM]I and their interaction with SO_2 in mode I : (d) [EMIM]Cl + SO_2 ($\Delta G_i = -11.1$ kcal/mol), (e) [EMIM]Br + SO_2 ($\Delta G_i = -10.7$ kcal/mol), (f) [EMIM]I + SO_2 ($\Delta G_i = -11.1$ kcal/mol) and in mode II : (g) [EMIM]Cl + SO_2 ($\Delta G_i = -11.3$ kcal/mol), (h) [EMIM]Br + SO_2 ($\Delta G_i = -11.5$ kcal/mol), (i) [EMIM]I + SO_2 ($\Delta G_i = -10.5$ kcal/mol).

that the absorption and desorption process of SO_2 in [BMIm]Cl was reversible. However, high desorption temperature was required for the cycle and the desorption rate was exceedingly slow even at 140 °C. It cannot be excluded that SO_2 is partially chemisorbed on ILs from the absorption-desorption experiment. The reversibility of SO_2 absorption in [BMIm]Cl was also monitored by FT-IR spectroscopy. Figure 2 shows the spectra of pure [BMIm]Cl, SO_2 absorbed [BMIm], and SO_2 desorbed [BMIm]. The broad band at about 3500 cm⁻¹ indicates the stretching peak of hydroxyl from water. Water was difficult to be removed from [BMIm]Cl. When SO_2 was absorbed in [BMIm]Cl, The band at about 3500 cm⁻¹ almost disappeared and new bands at 1137 and 1308 cm⁻¹ appeared. The stretching bands of S=O for SO_2 gas were observed at 1151 (v_1) and 1362 (v_3) cm⁻¹,[13] while those for SO_2 dissolved in hexane at 1148 (v_1) and 1338 (v_3) cm⁻¹.[14] The shift of the asymmetric band indicates that the bonding strength of S=O decreased by the interaction between SO_2 and [BMIm]Cl, when SO_2 was absorbed in [BMIm]Cl. In Raman spectra of [BMIm]Br-SO_2, it was observed that the symmetric stretching of SO_2 (v_1) exhibited a very strong band at

1138 cm⁻¹.[15] This shift to lower wavenumbers was explained as a consequence of electrostatic and charge-transfer (CT) effects between Br⁻ and SO_2.[16] On the other hand, no special changes in the bands of [BMIm]Cl were observed from the SO_2 absorption. When, SO_2 was desorbed at 140 °C, the band at about 3500 cm⁻¹ disappeared, indicating that water was removed with SO_2 during the desorption process. FT-IR studies clearly shows that the absorption and desorption process of SO_2 is reversible in [BMIm]Cl.

To explain the solubility behavior of SO_2 in various [EMIm]X (where X = Cl, Br, and I), theoretical investigation was conducted at the B3LYP level of the theory (6-31 + G* for C, H, N and O and LanL2DZ(ECP) for S, Cl, Br and I) using the Gaussian 03 program. The optimized structures showing the interactions of [EMIm]X with SO_2 are depicted in Figure 3. As can be deduced from the experimental results, there exists a substantial interaction between the basic halide anion, X⁻ and acidic center of SO_2. There exist two modes of interaction. In the mode I, SO_2 is trapped between imidazolium cation and halide anion where the oxygen is interacting with the imidazolium C_2-H
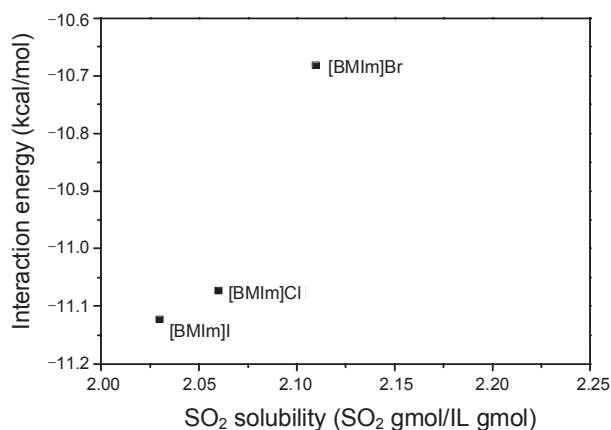
Figure 4. The relationship between the interaction energy of halide anion-SO_2 and SO_2 solubility.

and methyl part and sulfur is interacting with the halide. In the mode II, primary interaction of halide is with the imidazolium C_2-H and SO_2 is interacting with the halide anion. The free energies of interaction (ΔG_i) with SO_2 in mode I were calculated as −11.1, −10.7 and −11.1 kcal/mol for [EMIm]Cl, [EMIm]Br and [EMIm]I, respectively (see Figure 3-d, e and f) in the order of Cl ~ I > Br. Similar energies in mode II were calculated as −11.3, −11.5 and −10.5 kcal/mol for [EMIm]Cl, [EMIm]Br and [EMIm]I, respectively (see Figure 3-g, h and i) in the order of Br > Cl > I. The change in the magnitude of interaction depending on the mode of interaction can be presumably ascribed to the strength of interaction between the halide anion and the imidazolium C_2-H. Interaction with harder and smaller chloride ion is stronger than with softer and larger iodide ion. Therefore, to break the interaction with the imidazolium C_2-H and make a new interaction with SO_2 as in mode I, newly formed interaction must be stronger than the previous one. In case of chloride and bromide, this is not the situation and mode II is preferable to mode I. In case of iodide, the interaction between iodide and C_2-H is weak enough to break to form a new interaction, making mode I more preferable to mode II.

Figure 4 shows the relationship between the interaction energy and SO_2 solubility. As a whole, the order Br > Cl > I holds good and these computational results are in good agreement with the experimental absorption data.

Conclusion

Cationic and anionic effects of ILs were investigated using eight IL samples: [BMIm]Cl, [BMIm]Br, [BMIm]I, [EMIm]Cl, [HMIm]Cl, [OMIm]Cl, [BMpyri]Cl and [BMpyrr]Cl. The SO_2 solubility of ionic liquids with halide anions showed the solu

bility lies in the range 1.91 ~ 2.22 SO_2/ILs mol ratio. However, it can be concluded that ILs with halide anions follow the SO_2 solubility order Br > Cl > I. From theoretical points of view, two models were examined. In the mode I, SO_2 is trapped between imidazolium cation and halide anion where the oxygen is interacting with the imidazolium C_2-H and methyl part and sulfur is interacting with the halide. In the mode II, primary interaction of halide is with the imidazolium C_2-H and SO_2 is interacting with halide anion. The free energies of interaction (ΔG_i) with SO_2 in mode I were calculated as −11.1, −10.7 and −11.1 kcal/mol for [EMIm]Cl, [EMIm]Br and [EMIm]I, respectively in the order Cl ~ I > Br. Energy calculations in mode II were −11.3, −11.5 and −10.5 kcal/mol for [EMIm]Cl, [EMIm]Br and [EMIm]I, respectively in the order Br > Cl > I. Therefore, it has been concluded that model II was more preferable to model I which is consistent with the experimental results.

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