Absorption of SO\textsubscript{2} at High Temperatures by Ionic Liquids and the Absorption Mechanism

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The capture of SO\textsubscript{2} at or close to the temperatures of real flue gas is much more attractive in application. In this work, two kinds of ionic liquids (ILs) based on lactate anion were used to absorb SO\textsubscript{2} at high temperatures from 100 to 120 °C. The ILs show high absorption capacities of over one mol SO\textsubscript{2} per mol IL at 110 °C. The absorption of SO\textsubscript{2} by the ILs based on lactate anion is reversible and the ILs can be reused for the capture of SO\textsubscript{2} at high temperatures with high absorption capacity and thermal stability. Furthermore, the absorption mechanism of SO\textsubscript{2} by the ILs was studied by FT-IR, \textsuperscript{1}H NMR and \textsuperscript{31}P NMR spectra. It has been found that there are strong chemical interactions between the ILs and SO\textsubscript{2}. Also the absorption mechanism is different when there is water present in ILs compared to when there is not.

Key Words: Ionic liquids, SO\textsubscript{2}, High temperatures, Absorption, Mechanism

Introduction

The emission of sulfur dioxide (SO\textsubscript{2}), which is mainly from the burning of fossil fuels, has drawn much attention worldwide. It is essential to remove SO\textsubscript{2} from the flue gas since SO\textsubscript{2} is harmful to human body and causes serious environmental pollution. Up to now, flue gas desulfurization (FGD) is the most efficient way for the capture of SO\textsubscript{2}.\textsuperscript{1,2}

Currently, CaCO\textsubscript{3} is the most commonly used material for flue gas desulfurization (FGD), but there are large amounts of by-product CaSO\textsubscript{4} produced in the process. Liquid absorbents such as aqueous amines have also been used. However, this method may cause secondary pollution due to the high volatility of amines. As a result, recyclable liquid solvents with low volatility and high capacity are expected as excellent absorbents for the capture of SO\textsubscript{2}.

Recently, the absorption of acidic gases (CO\textsubscript{2}, SO\textsubscript{2} and H\textsubscript{2}S) by ionic liquids (ILs) has been widely studied for their unique properties. For example, ILs have negligible vapor pressure, high thermal stability, tunable structure and high absorption capacity of acidic gas. Han et al. reported the first task-specific ILs 1,1,3,3-tetramethylguanidinium lactate ([TMG]L) for the capture of SO\textsubscript{2}. They found that the mole ratio of SO\textsubscript{2} to [TMG]L could reach 1.0 at 40 °C with 8% SO\textsubscript{2} in N\textsubscript{2} for emission according to the technical code for designing flue gas desulfurization plants of fossil fuel power plants of China (DL/T 5196-2004). Therefore, there would be large amounts of energy consumption during the process. The capture of SO\textsubscript{2} at or close to the temperatures of real flue gas shows some advantages compared with the traditional method: (1) the energy cost of cooling down the high temperature flue gas would be decreased significantly; (2) heating the purified flue gas would no longer be needed. For their excellent properties, ILs can be used at high temperatures, and the ILs with high SO\textsubscript{2} absorption capacities at high temperatures are much more attractive in application. However, the previous studies mainly focused on SO\textsubscript{2} capture at low temperatures (some even at room temperature). These ILs cannot efficiently capture SO\textsubscript{2} at high temperatures. For example, the solubility of 0.1 MPa SO\textsubscript{2} in [TMG][BTA] at 120 °C is very low, just 0.1 mole SO\textsubscript{2} per mole IL.\textsuperscript{3} Therefore, it is necessary to design new ILs with high capacities to capture SO\textsubscript{2} at high temperatures. ILs cannot absorb large amounts of SO\textsubscript{2} by physical interactions at very high temperatures. So, it is reasonable to design ILs that can chemically interact with SO\textsubscript{2}. It has been reported that ILs based on lactate, acetate and methyl sulfate ether-functionalized imidazolium-based\textsuperscript{4-6}, amide-thiocyanates eutectic ILs\textsuperscript{7} and caprolactam tetrabutyl ammonium bromide,\textsuperscript{8-10} have been studied by different research groups. New technologies, such as ILs supported on membranes or porous silicon carbide silica and ILs polymers, have also been applied for the capture of SO\textsubscript{2}. Simultaneously, theoretical researches on the absorption of SO\textsubscript{2} by ILs have attracted much attention.

After removing dust, the temperature of real flue gas is around 140 °C.\textsuperscript{31} The flue gas with high temperature should be cooled down to about 50 °C for the capture of SO\textsubscript{2} in wet desulfurization process; and the purified flue gas should be heated to above 80 °C for emission according to the technical code for designing flue gas desulfurization plants of fossil fuel power plants of China (DL/T 5196-2004). Therefore, there would be large amounts of energy consumption during the process. The capture of SO\textsubscript{2} at or close to the temperatures of real flue gas shows some advantages compared with the traditional method: (1) the energy cost of cooling down the high temperature flue gas would be decreased significantly; (2) heating the purified flue gas would no longer be needed. For their excellent properties, ILs can be used at high temperatures, and the ILs with high SO\textsubscript{2} absorption capacities at high temperatures are much more attractive in application. However, the previous studies mainly focused on SO\textsubscript{2} capture at low temperatures (some even at room temperature). These ILs cannot efficiently capture SO\textsubscript{2} at high temperatures. For example, the solubility of 0.1 MPa SO\textsubscript{2} in [TMG][BTA] at 120 °C is very low, just 0.1 mole SO\textsubscript{2} per mole IL.\textsuperscript{3} Therefore, it is necessary to design new ILs with high capacities to capture SO\textsubscript{2} at high temperatures. ILs cannot absorb large amounts of SO\textsubscript{2} by physical interactions at very high temperatures. So, it is reasonable to design ILs that can chemically interact with SO\textsubscript{2}. It has been reported that ILs based on lactate, acetate and methyl sulfate ether-functionalized imidazolium-based\textsuperscript{4-6}, amide-thiocyanates eutectic ILs\textsuperscript{7} and caprolactam tetrabutyl ammonium bromide,\textsuperscript{8-10} have been studied by different research groups. New technologies, such as ILs supported on membranes or porous silicon carbide silica and ILs polymers, have also been applied for the capture of SO\textsubscript{2}. Simultaneously, theoretical researches on the absorption of SO\textsubscript{2} by ILs have attracted much attention.

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anions can chemically absorb \( \text{SO}_2 \). However, Lee et al. reported that the absorption of \( \text{SO}_2 \) by \([\text{Bmim}][\text{Ac}]\) is irreversible when there is water in the IL or in the gas. During the absorption process, the acetate anion in \([\text{Bmim}][\text{Ac}]\) transforms into acetic acid and the IL transforms into \([\text{Bmim}][\text{HOSO}_2]\). The acetic acid formed could be released from the IL easily due to its high volatility, which results in the non-renewable of \([\text{Bmim}][\text{Ac}]\). Considering the above result, lactic acid may be a wise choice as the anion of ILs due to its low vapor pressure.

In previous work, the absorption and desorption behaviors of \( \text{SO}_2 \) by lactate anion-based ILs with different kinds of cations were studied. It was found that tetraethylammonium-based IL shows the highest \( \text{SO}_2 \) absorption capacity and imidazolium-based IL shows the highest thermal stability. From the TGA curves of tetraethylammonium lactate \([\text{N}2222][\text{L}]\) and 1-butyl-3-methylimidazolium lactate \([\text{Bmim}][\text{L}]\), we know that the decomposition temperatures \( (T_d) \) for \([\text{N}2222][\text{L}]\) and \([\text{Bmim}][\text{L}]\) are 201 °C and 232 °C, respectively. As a result, \([\text{N}2222][\text{L}]\) and \([\text{Bmim}][\text{L}]\) can be used at temperatures higher than 100 °C. Although \([\text{N}2222][\text{L}]\) and \([\text{Bmim}][\text{L}]\) can absorb \( \text{SO}_2 \) efficiently at 60 °C, whether the ILs can be applied for the absorption of \( \text{SO}_2 \) at higher temperatures was not studied; neither was the absorption mechanism. Therefore, the absorption of \( \text{SO}_2 \) by \([\text{N}2222][\text{L}]\) and \([\text{Bmim}][\text{L}]\) at high temperatures from 100 °C to 120 °C were studied. Effects of temperature, \( \text{SO}_2 \) partial pressure and water on the absorption of \( \text{SO}_2 \) by the ILs were systematically investigated, and the absorption mechanism was proposed based on the FT-IR, \(^1\text{H} \) NMR and \(^13\text{C} \) NMR spectra.

### Experimental

**Raw Materials and Experimental Methods.** \( \text{SO}_2 \) (99.95%) and \( \text{N}_2 \) (99.999%) were obtained from Beijing Haipu Gases Co., Ltd. (Beijing, China). \( \text{N}2222 \) and \( \text{N}2222 \) were synthesized and characterized following the literature. The absorption and desorption of \( \text{SO}_2 \) were carried out at ambient pressure in a constant temperature oil bath. Before absorption, about 3.5 g IL was loaded in a glass tube, and the IL was treated with 100 cm\(^3\)/min \( \text{N}_2 \) at 110 °C for more than 12 h to remove volatile compounds. Then, some amount of the IL was drawn from the glass tube to ensure that 3.0 g IL was left in the glass tube. The absorption of \( \text{SO}_2 \) was treated with 50 cm\(^3\)/min \( \text{SO}_2 \), and the desorption of \( \text{SO}_2 \) was treated with 100 cm\(^3\)/min \( \text{N}_2 \) at desired temperatures. Solubility of \( \text{SO}_2 \) in the ILs was determined by weight increase of the glass tube.

The absorption of \( \text{SO}_2 \) in ILs + \( \text{H}_2\text{O} \) \((w_{\text{IL}} = 83\%)\) was carried out on the same device at 45 °C because it is difficult to control water steam, and the solubility of \( \text{SO}_2 \) in ILs + \( \text{H}_2\text{O} \) cannot be determined exactly at high temperatures. During the absorption, water might be released from the absorption glass tube. To capture the released water, the down stream gas from the absorption glass tube was bubbled through a concentrated sulfuric acid solution in a glass tube. The water absorbed by the concentrated sulfuric acid was also considered when determining the solubility of \( \text{SO}_2 \) in the ILs with water.

### Results and Discussion

**Effect of Temperature and \( \text{SO}_2 \) Partial Pressure on the Absorption of \( \text{SO}_2 \).** Figure 1 shows the absorption of \( \text{SO}_2 \) in \([\text{N}2222][\text{L}]\) and \([\text{Bmim}][\text{L}]\) at 100, 110 and 120 °C. It can be seen from the figures that the ILs can absorb \( \text{SO}_2 \) with high efficiency and the absorption curves almost increase linearly in the initial 5 minute period. The ILs can absorb large amounts of \( \text{SO}_2 \) even at high temperatures. For example, the mole ratios of \( \text{SO}_2 \) to \([\text{N}2222][\text{L}]\) are 1.229, 1.138 and 1.075 at 100, 110 and 120 °C, respectively. The \( \text{SO}_2 \) absorption capacities of the ILs from 25 to 120 °C shows that \([\text{Bmim}][\text{L}]\) has a slightly smaller absorption capacity than \([\text{N}2222][\text{L}]\) does (Figure S1), such as at 100 °C 1.102 mole ratio of \( \text{SO}_2 \) to IL for the former, and 1.229 for the latter. Effect of \( \text{SO}_2 \) partial pressure on the absorption capacities of the ILs is shown in

![Figure 1](image_url)
Figure 2, which shows that the mole ratios of \( \text{SO}_2 \) to [N\text{2222}]L and [Bmim]L decrease from 1.138 and 1.033 to 0.547 and 0.456, respectively, when the partial pressure of \( \text{SO}_2 \) decreases from 101 kPa to 3 kPa. As a result, the absorption capacities of the ILs decrease with the increase of temperature and decrease of \( \text{SO}_2 \) partial pressure, which suggests that the ILs can be regenerated by increasing temperature and/or decreasing pressure.

**Desorption of \( \text{SO}_2 \) and Regeneration of the ILs.** The ILs saturated with \( \text{SO}_2 \) at 110 °C were treated with 100 cm\(^3\)/min \( \text{N}_2 \) at 110 °C. The absorbed \( \text{SO}_2 \) in the ILs can be released easily from the ILs in the initial 60 minute period, but then over time the mole ratio of \( \text{SO}_2 \) to IL changes slowly. Taking [Bmim]L as an example, the mole ratio of \( \text{SO}_2 \) to IL is 1.033, 0.330 and 0.157 at 0, 60 and 360 min, respectively. That is to say about 68% and 85% of the absorbed \( \text{SO}_2 \) can be released from the IL if treated with 100 cm\(^3\)/min \( \text{N}_2 \) at 110 °C for 60 and 360 min. Under this condition, it needs a long time to release \( \text{SO}_2 \) from the ILs. However, the desorption efficiency can be enhanced by treating the \( \text{SO}_2 \) absorbed ILs at higher temperatures and/or lower pressures. The FT-IR spectra of the ILs before absorption and after desorption are shown in Figure S2, which confirms that the ILs can be regenerated by heating the ILs saturated with \( \text{SO}_2 \).

Figure 3 shows the reuse cycles of [N\text{2222}]L and [Bmim]L for \( \text{SO}_2 \) absorption/desorption. The absorption of \( \text{SO}_2 \) was carried out at 110 °C for 60 min, and the desorption of \( \text{SO}_2 \) was carried out at 110 °C for 360 min. It can be seen from Figure 3 that no obvious loss of absorption capacities were found for the ILs during the reuse cycles. Taking [Bmim]L as an example, the mole ratios of \( \text{SO}_2 \) to IL of the 5 cycles are 1.033, 1.031, 1.043, 1.045, 1.029 after the absorption at 110 °C for 60 min. As a result, the absorption of \( \text{SO}_2 \) by the ILs are reversible and the ILs can be reused for the capture of \( \text{SO}_2 \) with high absorption capacity and stability.

**Effect of Water on the Absorption of \( \text{SO}_2 \) and Regeneration of the ILs.** There is some amount of water or moisture in flue gas, and the IL will absorb water from flue gas due to their hydrophilicity. Previously, Lee et al. reported that in the presence of water, the absorption of \( \text{SO}_2 \) in [Bmim][Ac] is irreversible for the high volatility of acetic acid.\(^{14}\) As a result, lactic acid with low vapor pressure may solve the problem.

In order to verify our hypothesis, the absorption of pure \( \text{SO}_2 \) in IL + H\(_2\)O (w\(_\text{IL} = 83\%\)) and regeneration of the ILs were studied. The absorption of \( \text{SO}_2 \) was carried out at 45 °C for 60 min and the desorption of \( \text{SO}_2 \) was carried out at 45 °C for 60 min (It is very dangerous to put the glass tube with large amounts of \( \text{SO}_2 \) into the oil bath at 110 °C directly) and then at 110 °C for 360 min, and the result is shown in Figure 4. The \( \text{SO}_2 \) absorption capacities of ILs in the presence of water decrease a little. For example, the mole ratio of \( \text{SO}_2 \) to [Bmim]L is 1.629 when there is 17 wt % water in the IL, compared with that of 1.940 when there is no water. There are strong interactions between hydrophilic ILs and water, and the interactions between the ILs and \( \text{SO}_2 \) decrease with the addition of water. As a result, the competition between water and \( \text{SO}_2 \) leads to the decrease of \( \text{SO}_2 \) absorption capacities of ILs in the presence of water.

Figure 5 shows the absorption and desorption of \( \text{SO}_2 \) by the two ILs in the presence of 17 wt % water with 5 cycles. The results indicate that the absorption of \( \text{SO}_2 \) by the ILs based on lactate anion are highly reversible in the presence of water. For example, the mole ratios of \( \text{SO}_2 \) to [Bmim]L...
are 1.629, 1.637, 1.621, 1.638 and 1.614 of the 5 cycles of absorption. It is very interesting that the absorption of SO$_2$ by [Bmim][Ac] is irreversible while that of [Bmim]L is highly reversible, though the two ILs have the same cation [Bmim]$^+$. The reason is that after the absorption of SO$_2$ by the ILs in the presence of water, the formed acetic acid could be easily removed under vacuum at high temperature, while the formed lactic acid would remain in the absorbent. After the absorbed SO$_2$ is released from the absorbent, [Bmim]L can be regenerated by the combination of [Bmim]$^+$ and lactate anion. The result suggests that an acid with low vapor pressure is favorable to form excellent ILs which could be used in real flue gas.

The Absorption Mechanism. The high SO$_2$ absorption capacities of the ILs at high temperatures suggests that strong chemical interactions existed between SO$_2$ and the ILs. The absorption mechanism of SO$_2$ by ILs has been studied experimentally and theoretically. Han et al. demonstrated that both physical and chemical interactions existed between SO$_2$ and [TMG]L. They suggested that SO$_2$ reacted with the N–H group in [TMG]$^+$ and a new N–S band was formed, so one mole IL can chemically absorb one mole SO$_2$. Zhang et al. reported new ILs based on [TMG]$^+$, and they suggested a similar absorption mechanism. Zhang et al. and Zhai et al. proposed that SO$_2$ reacted with the N–H group on the cation of alkanolaminium-based ILs, while the O atom on S=O probably forms intramolecular hydrogen bond with the H atom of the amine. Simultaneously, a carboxylic acid such as formic acid, acetic acid and lactic acid was formed. Recently, Wu et al. demonstrated that the task-specific ILs, [TMG]L and [MEA]L, could chemically absorb 0.5 mol SO$_2$ per mole IL, and they distinguished the physically and chemically absorbed SO$_2$ and confirmed the absorption mechanism. Lee et al. found that [Bmim][Ac] would change into [Bmim][HOSO$_2$] after the absorption of SO$_2$ when there was some amount of water in the IL or in the gas. Wang et al. applied molecular dynamics simulations and quantum chemical calculations to investigate the solubility of SO$_2$ in [TMG]L. The theoretical research shows that SO$_2$ could form S⋯O interactions with lactate anion and form N–H⋯O interactions with [TMG]$^+$. The S⋯O interactions are 3.5–8.8 times stronger than that of N–H⋯O hydrogen bonding, which suggests that the chemically absorbed SO$_2$ was mainly due to the strong interactions between SO$_2$ and electronegative oxygen atoms in the anion. Based on the theory, Wang et al. synthesized quaternary phosphonium-based ILs with multiple electronegative nitrogen atoms in the anions. As expected, these ILs have extremely high absorption capacities. Although many groups have studied the absorption mechanism of SO$_2$ by ILs, the mechanism is
still unclear.

In order to understand the absorption mechanism of SO\(_2\) by [N\(_{2222}\)]L and [Bmim]L, the ILs and ILs-SO\(_2\) were characterized by FT-IR (KBr), \(^1\)H NMR (CDCl\(_3\)) and \(^{13}\)C NMR (DMSO-d\(_6\)). The FT-IR, \(^1\)H NMR and \(^{13}\)C NMR spectra of [N\(_{2222}\)]L and [N\(_{2222}\)]L-SO\(_2\) are shown in Figure 6. Compared with the FT-IR spectrum of [N\(_{2222}\)]L, the spectrum of [N\(_{2222}\)]L-SO\(_2\) shows new absorption bands at 1224 cm\(^{-1}\) and 967 cm\(^{-1}\), which can be assigned to sulphate S=O and S–O stretches, respectively. This could support the existence of chemical interactions between SO\(_2\) and the IL. The newly appeared band at 1731 cm\(^{-1}\) shows the formation of –COOH. Since there is no H\(^+\) in the system (IL or SO\(_2\)) that can be supplied to –COO\(^–\) to form –COOH, the production of H\(^+\) during the reaction of IL and SO\(_2\) is necessary. It can be seen from the \(^1\)H NMR spectra of [N\(_{2222}\)]L and [N\(_{2222}\)]L-SO\(_2\) that the typical peak of –CH(OH)– of lactate anion moves downfield from 3.84 ppm to 4.52 ppm, which suggests that the IL can chemically absorb SO\(_2\) and the strong interactions exist between SO\(_2\) and lactate anion. From the \(^{13}\)C NMR spectra of [N\(_{2222}\)]L and [N\(_{2222}\)]L-SO\(_2\), we can see that the peaks of CH\(_3\)–, –CH(OH)– and –COO\(^–\) of lactate anion moves upfield from 21.5, 67.3 and 177.9 ppm to 19.5, 63.2 and 175.6 ppm, respectively, which confirms that SO\(_2\) reacts with lactate anion. The results of FT-IR, \(^1\)H NMR and \(^{13}\)C NMR spectra of [Bmim]L before and after SO\(_2\) absorption (Figure S3) also show that the IL could chemically absorb SO\(_2\), and SO\(_2\) reacts with lactate anion. Based on the above results, we proposed that SO\(_2\) reacts with –OH to from –O–(S=O)–O– and H\(^+\) (Scheme 1). It is similar to the reactions of SO\(_2\) and alcoholic hydroxyl group to form zwitterionic compounds reported by other research groups.\(^{36-39}\) When there is water in the IL or in the gas, SO\(_2\) reacts with water and forms H\(_2\)SO\(_3\). Since lactic acid (pK\(_{a}\) = 3.86) is a weaker acid than H\(_2\)SO\(_3\) (pK\(_{a1}\) = 1.89), the conjugated base (lactate anion) would be favorable to exist as lactic acid in the presence of H\(_2\)SO\(_3\). As a result, the IL reacts with H\(_2\)SO\(_3\) to form [IL]\(^+\)HSO\(_3^–\)/[IL]\(^2+\)SO\(_3^{2–}\) and lactic acid (Scheme 1).

### Conclusion

In summary, two kinds of ILs based on lactate anion were used to absorb SO\(_2\) at high temperatures more than 100 °C. Effects of temperature, SO\(_2\) partial pressure and water on the absorption of SO\(_2\) by [N\(_{2222}\)]L and [Bmim]L were studied. Furthermore, the absorption mechanism of SO\(_2\) by the ILs was studied by FT-IR, \(^1\)H NMR and \(^{13}\)C NMR spectra. It was found that, the mole ratio of SO\(_2\) to the ILs can reach more than 1.00 at 110 °C. The absorption/desorption cycles

![Figure 6](image-url)
of SO$_2$ by these ILs were tested for five runs, and no obvious loss of absorption capacities were found even when there is some amount of water in ILs during the cycles. The result shows that the ILs based on lactate anion are promising absorbents for the capture of SO$_2$ at high temperatures with high absorption capacity and stability. The absorption mechanism has been proposed, indicating that there are strong chemical interactions between the ILs and SO$_2$.

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