Absorption of SO$_2$ at High Temperatures by Ionic Liquids and the Absorption Mechanism

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The capture of SO$_2$ 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$_2$ at high temperatures from 100 to 120 °C. The ILs show high absorption capacities of over one mol SO$_2$ per mol IL at 110 °C. The absorption of SO$_2$ by the ILs based on lactate anion is reversible and the ILs can be reused for the capture of SO$_2$ at high temperatures with high absorption capacity and thermal stability. Furthermore, the absorption mechanism of SO$_2$ by the ILs was studied by FT-IR, ^{1}H NMR and ^{13}C NMR spectra. It has been found that there are strong chemical interactions between the ILs and SO$_2$. Also the absorption mechanism is different when there is water present in ILs compared to when there is not.

Key Words : Ionic liquids, SO$_2$, High temperatures, Absorption, Mechanism

Introduction

The emission of sulfur dioxide (SO$_2$), which is mainly from the burning of fossil fuels, has drawn much attention worldwide. It is essential to remove SO$_2$ from the flue gas since SO$_2$ 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$_2$.[1, 2]

Currently, CaCO$_3$ is the most commonly used material for flue gas desulfurization (FGD), but there are large amounts of by-product CaSO$_4$ 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$_2$.

Recently, the absorption of acidic gases (CO$_2$, SO$_2$ and H$_2$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$_2$. They found that the mole ratio of SO$_2$ to [TMG]L could reach 1.0 at 40 °C with 8% SO$_2$ in N$_2$.[3] From the viewpoint of application, Wu *et al.* studied the effect of water and O$_2$ on the absorption of SO$_2$ by functional ILs, and they proposed a way to regenerate the ILs.[4-6] Zhang *et al.* reported new guanidinium-based ILs with quite low viscosities for the capture of SO$_2$.[7] Riisager *et al.* found that [TMG][BF$_4$], [TMG][BTA], [TMGB$_2$][BTA], [Bmim][BF$_4$] and [Bmim][BTA] could absorb large amounts of SO$_2$ through physical absorption.[8] Other types of ILs, such as imidazolium-based,[9-16] alkanolaminium-based,[17-19] quaternary phosphonium-based,[16,20] ether-functionalized imida-

zolium-based[15,16] ILs, amide-thiocyanates eutectic ILs[21] and caprolactam tetrabutyl ammonium bromide,[22-24] have been studied by different research groups. New technologies, such as ILs supported on membranes or porous silica particles and ILs polymers, have also been applied for the capture of SO$_2$.[25-27] Simultaneously, theoretical researches on the absorption of SO$_2$ by ILs have attracted much attention.[28-30]

After removing dust, the temperature of real flue gas is around 140 °C.[31] The flue gas with high temperature should be cooled down to about 50 °C for the capture of SO$_2$ 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$_2$ 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$_2$ absorption capacities at high temperatures are much more attractive in application. However, the previous studies mainly focused on SO$_2$ capture at low temperatures (some even at room temperature). These ILs cannot efficiently capture SO$_2$ at high temperatures. For example, the solubility of 0.1 MPa SO$_2$ in [TMG][BTA] at 120 °C is very low, just 0.1 mole SO$_2$ per mole IL.[8] Therefore, it is necessary to design new ILs with high capacities to capture SO$_2$ at high temperatures. ILs cannot absorb large amounts of SO$_2$ by physical interactions at very high temperatures. So, it is reasonable to design ILs that can chemically interact with SO$_2$. It has been reported that ILs based on lactate, acetate and methyl sulfate

anions can chemically absorb SO_2.[20] However, Lee *et al.* reported that the absorption of SO_2 by [Bmim][Ac] is irreversible when there is water in the IL or in the gas.[14] During the absorption process, the acetate anion in [Bmim][Ac] transforms into acetic acid and the IL transforms into [Bmim][$HOSO_2$]. The acetic acid formed could be released from the IL easily due to its high volatility, which results in the non-renewable of [Bmim][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 SO_2 by lactate anion-based ILs with different kinds of cations were studied.[32] It was found that tetraethylammonium-based IL shows the highest SO_2 absorption capacity and imidazolium-based IL shows the highest thermal stability. From the TGA curves of tetraethylammonium lactate ([N_{2222}]L) and 1-butyl-3-methylimidazolium lactate ([Bmim]L), we know that the decomposition temperatures (T_d) for [N_{2222}]L and [Bmim]L are 201 ℃ and 232 ℃, respectively.[32] As a result, [N_{2222}]L and [Bmim]L can be used at temperatures higher than 100 ℃. Although [N_{2222}]L and [Bmim]L can absorb SO_2 efficiently at 60 ℃, whether the ILs can be applied for the absorption of SO_2 at higher temperatures was not studied; neither was the absorption mechanism. Therefore, the absorption of SO_2 by [N_{2222}]L and [Bmim]L at high temperatures from 100 ℃ to 120 ℃ were studied. Effects of temperature, SO_2 partial pressure and water on the absorption of SO_2 by the ILs were systematically investigated, and the absorption mechanism was proposed based on the FT-IR, ^{1}H NMR and ^{13}C NMR spectra.

Experimental

Raw Materials and Experimental Methods. SO_2 (99.95%) and N_2 (99.999%) were obtained from Beijing Haipu Gases Co., Ltd. (Beijing, China). *N*-Methylimidazole was obtained from Leadership Chemical Co., Ltd. (Shandong, China) and it was distilled before use. Analytical reagent lactic acid (85% in water), 1-chlorobutane (98%), sodium hydroxide (98%) and tetraethyl ammonium hydroxide (25% in water) were supplied by Aladdin Chemical Co., Ltd. (Shanghai, China). [N_{2222}]L and [Bmim]L were synthesized and characterized following the literature.[32]

The absorption and desorption of 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 N_2 at 110 ℃ for more than 12 h to remove volatile compounds.[33] 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 SO_2 was treated with 50 cm^3/min SO_2, and the desorption of SO_2 was treated with 100 cm^3/min N_2 at desired temperatures. Solubility of SO_2 in the ILs was determined by weight increase of the glass tube.

The absorption of SO_2 in ILs + H_2O (w_{IL} = 83%) was carried out on the same device at 45 ℃ because it is difficult to control water steam, and the solubility of SO_2 in ILs +

H_2O 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 SO_2 in the ILs with water.

Results and Discussion

Effect of Temperature and SO_2 Partial Pressure on the Absorption of SO_2. Figure 1 shows the absorption of SO_2 in [N_{2222}]L and [Bmim]L at 100, 110 and 120 ℃. It can be seen from the figures that the ILs can absorb 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 SO_2 even at high temperatures. For example, the mole ratios of SO_2 to [N_{2222}]L are 1.229, 1.138 and 1.075 at 100, 110 and 120 ℃, respectively. The SO_2 absorption capacities of the ILs from 25 to 120 ℃ shows that [Bmim]L has a slightly smaller absorption capacity than [N_{2222}]L does (Figure S1), such as at 100 ℃ 1.102 mole ratio of SO_2 to IL for the former, and 1.229 for the latter. Effect of SO_2 partial pressure on the absorption capacities of the ILs is shown in
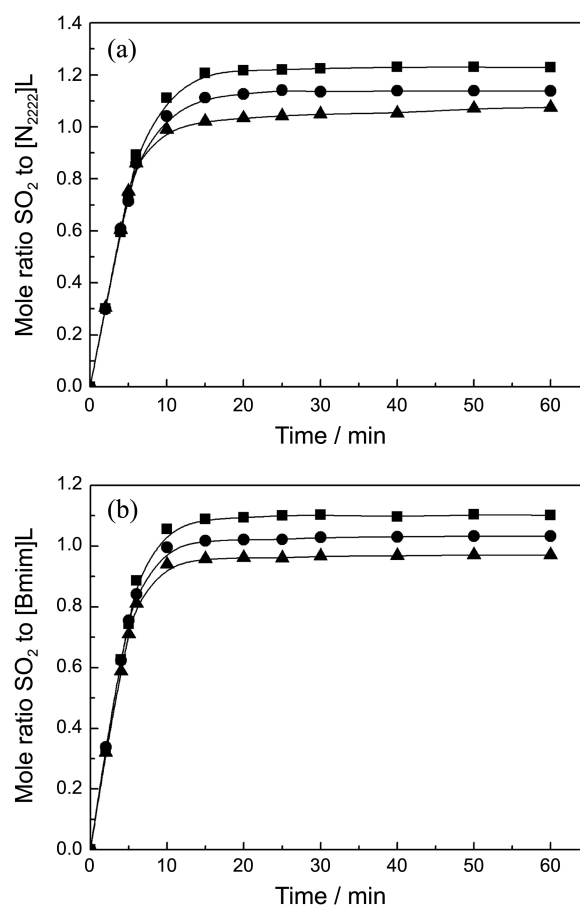

Figure 1. Absorption of SO_2 in (a) [N_{2222}]L and (b) [Bmim]L at high temperatures: ■, 100 ℃; ●, 110 ℃; ▲, 120 ℃.
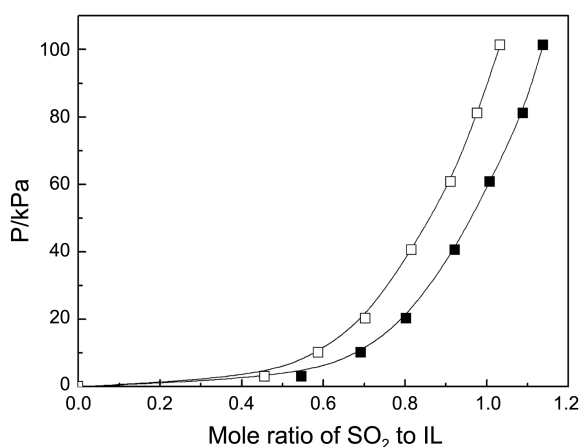
Figure 2. Effect of SO_2 partial pressure on the absorption capacities of the ILs at 110 °C: ■, $[N_{2222}]L$; □, [Bmim]L.

Figure 2, which shows that the mole ratios of SO_2 to $[N_{2222}]L$ and [Bmim]L decrease from 1.138 and 1.033 to 0.547 and 0.456, respectively, when the partial pressure of SO_2 decreases from 101 kPa to 3 kPa. As a result, the absoprtion capacities of the ILs decrease with the increase of temperature and decrease of SO_2 partial pressure, which suggests that the ILs can be regenerated by increasing temperature and/or decreasing pressure.

Desorption of SO_2 and Regeneration of the ILs. The ILs saturated with SO_2 at 110 °C were treated with 100 cm³/min N_2 at 110 °C. The absorbed 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 SO_2 to IL changes slowly. Taking [Bmim]L as an example, the mole ratio of 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 SO_2 can be released from the IL if treated with 100 cm³/min N_2 at 110 °C for 60 and 360 min. Under this condition, it needs a long time to release SO_2 from the ILs. However, the desorption efficiency can be enhanced by treating the 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 SO_2.

Figure 3 shows the reuse cycles of $[N_{2222}]L$ and [Bmim]L for SO_2 absorption/desorption. The absorption of SO_2 was carried out at 110 °C for 60 min, and the desorption of 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 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 SO_2 by the ILs are reversible and the ILs can be reused for the capture of SO_2 with high absorption capacity and stability.

Effect of Water on the Absorption of 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.*
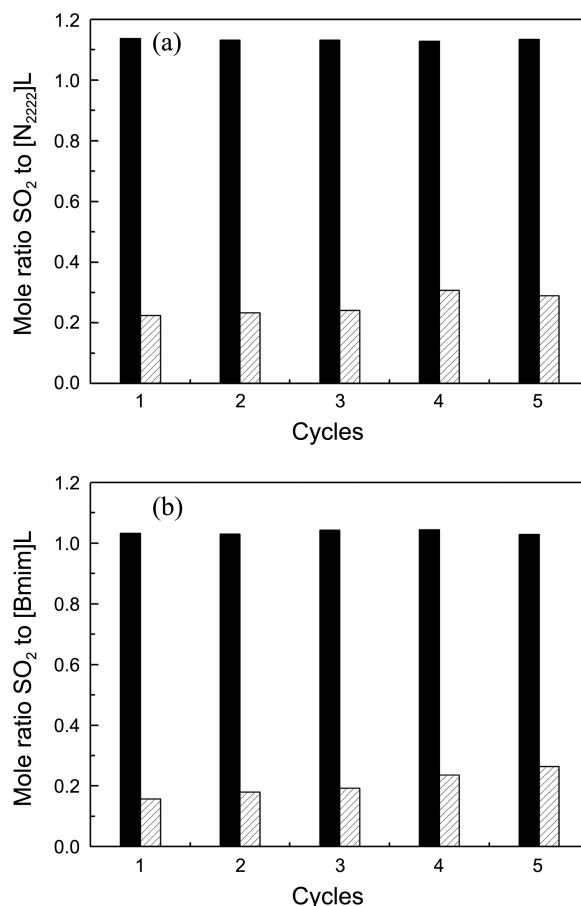

Figure 3. The absorption and desorption cycles of SO_2 in (a) $[N_{2222}]L$ and (b) [Bmim]L: ■, absorption; ▨, desorption.

reported that in the presence of water, the absorption of 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 SO_2 in IL + H_2O (w_{IL} = 83%) and regeneration of the ILs were studied. The absorption of SO_2 was carried out at 45 °C for 60 min and the desorption of SO_2 was carried out at 45 °C for 60 min (It is very dangerous to put the glass tube with large amounts of 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 SO_2 absorption capacities of ILs in the presence of water decrease a little. For example, the mole ratio of 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 SO_2 decrease with the addition of water. As a result, the competition between water and SO_2 leads to the decrease of SO_2 absorption capacities of ILs in the presence of water.

Figure 5 shows the absorption and desorption of SO_2 by the two ILs in the pesence of 17 wt % water with 5 cycles. The results indicate that the absorption of SO_2 by the ILs based on lactate anion are highly reversible in the presence of water. For example, the mole ratios of SO_2 to [Bmim]L
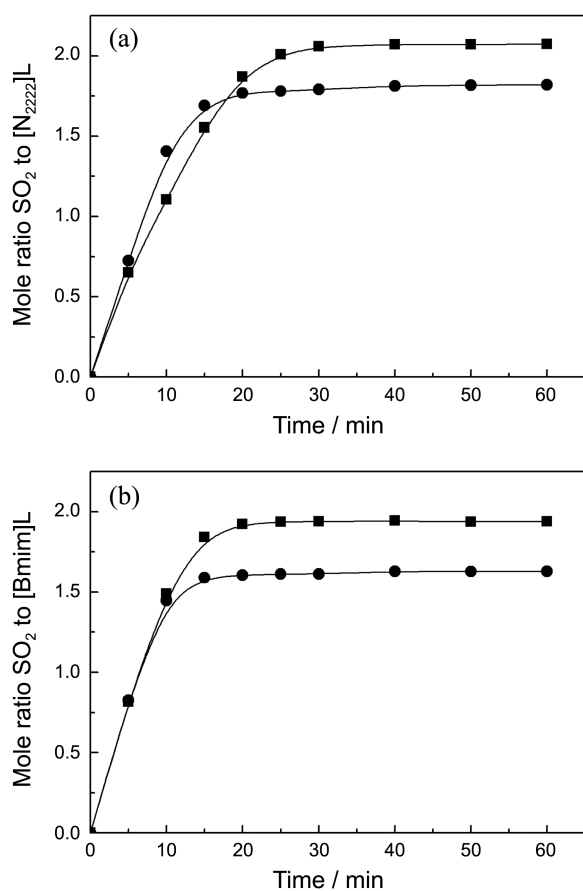
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Figure 4. The absorption of SO$_2$ in (a) [N$_{2222}$]L and (b) [Bmim]L at 45 °C: ■, IL; ● IL + H$_2$O (w_{IL} = 83%).

Figure 5. The absorption and desorption cycles of SO$_2$ in (a) [N$_{2222}$]L + H$_2$O (w_{IL} = 83%) and (b) [Bmim]L + H$_2$O (w_{IL} = 83%): ■, absorption; ▨, desorption.

are 1.629, 1.637, 1.621, 1.638 and 1.614 of the 5 cycles of absorption. It is very interesting that the absoption 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 machanism 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.[3] 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.[7] Zhang *et al.*[17] and Zhai *et al.*[18] proposed that SO$_2$ reacted with the N–H group on the cation of alkanolaminium-based ILs, while
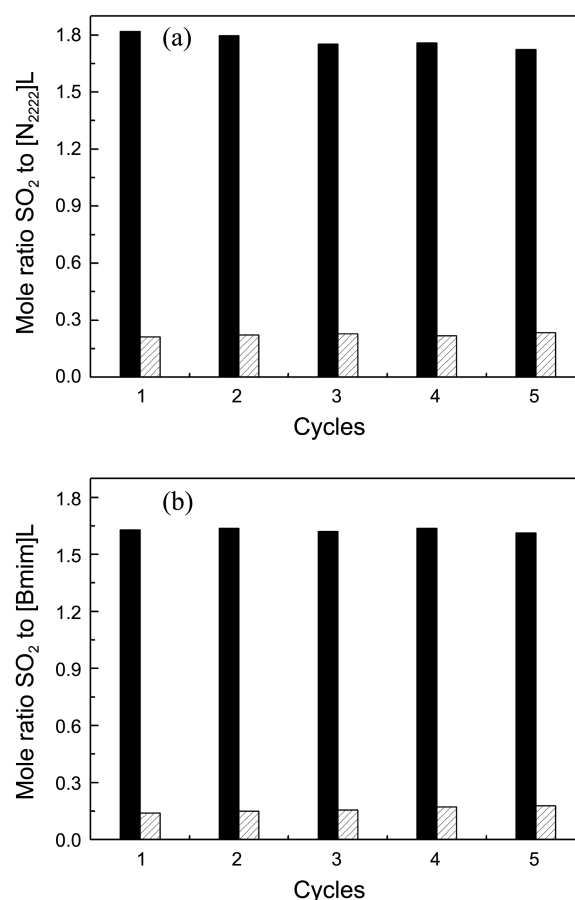
the O atom on S=O probably forms intramolecular hydrogen bond with the H atom of the amine. Simultaneously, a carboxylic acid such as formic acid, acetic acid and lactic acid was formed. Recently, Wu *et al.* demonstrated that the task-specific ILs, [TMG]L and [MEA]L, could chemically absorb 0.5 mol SO$_2$ per mole IL,[34] and they distinguished the physically and chemically absorbed SO$_2$ and confirmed the absorption mechanism.[35] 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.[14] Wang *et al.* applied molecular dynamics simulations[28] and quantum chemical calculations[29] 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 is 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.[20] 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
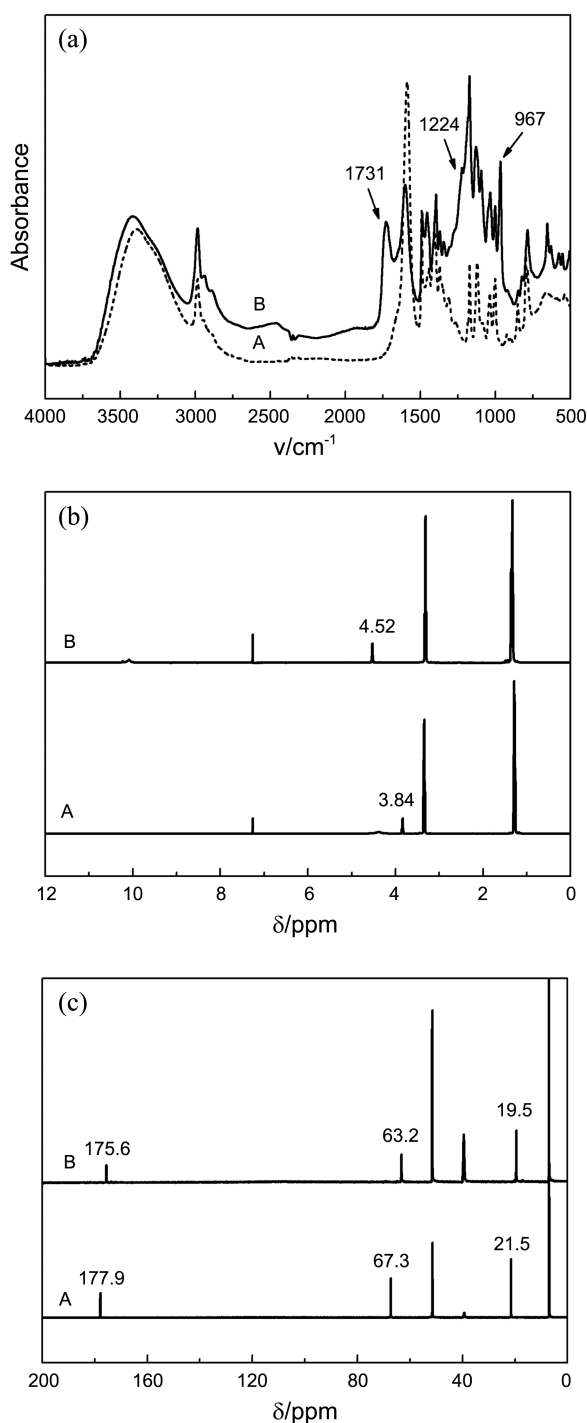
Figure 6. The (a) FT-IR, (b) ^{1}H NMR and (c) ^{13}C NMR spectra of [N₂₂₂₂]L before and after absorption: A, [N₂₂₂₂]L; B, [N₂₂₂₂]L-SO₂.

still unclear.

In order to understand the absorption mechanism of SO₂ by [N₂₂₂₂]L and [Bmim]L, the ILs and ILs-SO₂ were characterized by FT-IR (KBr), ^{1}H NMR (CDCl₃) and ^{13}C NMR (DMSO-d6). The FT-IR, ^{1}H NMR and ^{13}C NMR spectra of [N₂₂₂₂]L and [N₂₂₂₂]L-SO₂ are shown in Figure 6. Compared with the FT-IR spectrum of [N₂₂₂₂]L, the spectrum of [N₂₂₂₂]L-SO₂ 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 SO₂ and the IL. The newly appeared band at 1731 cm⁻¹ shows the the formation of –COOH. Since there is no H⁺ in the system (IL or SO₂) that can be supplied to –COO⁻ to form –COOH, the production of H⁺ during the reaction of IL and SO₂ is necessary. It can be seen from the ^{1}H NMR spectra of [N₂₂₂₂]L and [N₂₂₂₂]L-SO₂ 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 SO₂ and the strong interactions exist between SO₂ and lactate anion. From the ^{13}C NMR spectra of [N₂₂₂₂]L and [N₂₂₂₂]L-SO₂, we can see that the peaks of CH₃–, –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 SO₂ reacts with lactate anion. The results of FT-IR, ^{1}H NMR and ^{13}C NMR spectra of [Bmim]L before and after SO₂ absorption (Figure S3) also show that the IL could chemically absorb SO₂, and SO₂ reacts with lactate anion. Based on the above results, we proposed that SO₂ reacts with –OH to from –O–(S=O)–O⁻ and H⁺ (Scheme 1). It is similar to the reactions of SO₂ 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, SO₂ reacts with water and forms H₂SO₃. Since lactic acid (pK_a = 3.86) is a weaker acid than H₂SO₃ (pK_{a1} = 1.89), the conjugated base (lactate anion) would be favorable to exist as lactic acid in the presence of H₂SO₃. As a result, the IL reacts with H₂SO₃ to form [IL]⁺HSO₃⁻/[IL]₂²⁺SO₃²⁻ and lactic acid (Scheme 1).
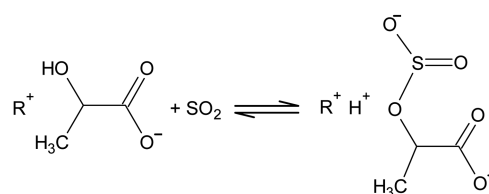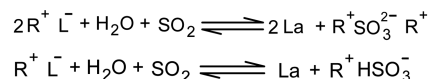
Scheme 1. The proposed absorption mechanism by the ILs based on lactate anion. R⁺ stands for [N₂₂₂₂]⁺ or [Bmim]⁺; L⁻ stands for lactate anion; La stands for lactate acid.

Conclusion

In summary, two kinds of ILs based on lactate anion were used to absorb SO₂ at high temperatures more than 100 °C. Effects of temperature, SO₂ partial pressure and water on the absorption of SO₂ by [N₂₂₂₂]L and [Bmim]L were studied. Furthermore, the absorption mechanism of SO₂ by the ILs was studied by FT-IR, ^{1}H NMR and ^{13}C NMR spectra. It was found that, the mole ratio of SO₂ to the ILs can reach more than 1.00 at 110 °C. The absorption/desorption cycles

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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