Absorption and Conversion of SO₂ in Functional Ionic Liquids: Effect of Water on the Claus Reaction

Yucui Hou, Qi Zhang, Minjie Gao, Shuhang Ren, and Weize Wu*

ABSTRACT: The absorption of SO₂ from flue gas and its conversion to chemicals is important in the industry. Functional ionic liquids (ILs) have been broadly used to absorb SO₂ in flue gas, but seldom convert it to chemicals. As we know, water is inevitable in a desulfurization process. In this work, three functional ILs (monoethanolammonium lactate-[MEA][Lac], 1,1,3,3-tetramethylguanidinium lactate-[TMG][Lac], tetraethylammonium lactate-[N_{2222}][Lac]) with or without water were used as absorbents to absorb SO₂ in flue gas, and then the absorbed SO₂ in the absorbents was converted to sulfur via a Claus reaction. The result shows that the three ILs can efficiently absorb SO₂ and convert it to sulfur. But the addition of water in the ILs can reduce the conversion of absorbed SO₂, and the conversion increases with increasing the acidity of absorbents. To explain this phenomenon, we studied the Claus reaction in H₂SO₃, NaHSO₃ and Na₂SO₃ aqueous solutions. It turns out that the conversion of the Claus reaction is related to the species of S (IV) in the order of the oxidability: H₂SO₃ > HSO₃⁻ > SO₃²⁻, and their proportions dependent on the pH of solutions. On the basis of the absorption mechanism of SO₂ in functional ILs aqueous solution, H₂S reacts with HSO₃⁻ and SO₃²⁻ with weaker oxidability, resulting in the lower conversion. Importantly, we found that the addition of lactic acid could increase the conversion of SO₂ via the Claus reaction.

1. INTRODUCTION

The emission of sulfur dioxide (SO₂), which is mainly emitted from burning of coal, brings harm to not only the human body but also environmental safety. Traditional flue gas desulfurization technologies, for example, limestone scrubbing, are deficient in absorbents regeneration and SO₂ utilization. Ionic liquids (ILs), which have many superior properties, have been widely studied in gas separation. Besides, ILs are promising reaction mediums because of their inherent catalytic reactivity for numerous reactions. Among them, functional ILs with some special groups can chemically absorb SO₂ so that SO₂ with low concentrations (like 0.2 vol %) in flue gas can be removed efficiently. Among functional ILs, functional ILs are quite strong, which make it difficult to be regenerated. Therefore, the desorption of SO₂ from functional ILs by high temperature treatment usually needs high energy consumption. Moreover, high temperature treatment also causes decreasing stability of absorbents and increasing difficulty of separation. Huang et al. performed good work to use various common ILs as the solvents for the Claus reaction, which could achieve a conversion rate up to 99% at 40 °C. However, more commonly studied ILs can absorb SO₂ with high solubility at high SO₂ concentrations only by physical interaction. To change the traditional method, our research group put forward a new method to regenerate functional ILs by using the Claus reaction and achieved good results. The result shows that the SO₂-absorbed functional ILs can be regenerated efficiently under a mild condition, and then SO₂ from flue gas can be converted to sulfur for the comprehensive utilization. After several absorption and regeneration cycles, the absorbents still have high absorption capacity of SO₂ and the conversion of SO₂ via the Claus reaction does not decrease significantly. This new regeneration method is easy to operate and shows a good prospect in application.

In the previous work, it has been found that H₂O has an effect on the liquid-phase Claus reaction. For monoethanolammonium lactate ([MEA][Lac]) used as an absorbent, the addition of H₂O can reduce the conversion of absorbed SO₂ via the Claus reaction, which is unfavorable to the regeneration process. However, no matter in the absorption or desorption processes, H₂O is an important component. There is about 7 vol % H₂O in flue gas at 40 °C, so absorbents contain a certain amount of water. In the Claus reaction, H₂O is a product of...
The absorption of SO₂ in ILs is that SO₂ is absorbed physically and chemically. The physical absorption follows Henry's law. The chemical absorption, taking [N₂₂₂₂][Lac] as an example, follows the reaction as shown in eq 1:29

\[ [\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{Lac}] + \text{SO}_2 \rightleftharpoons [\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{Lac}] \cdots \text{SO}_2 \]  

(1)

It can be seen from Table 1 that the absorption of SO₂ does not reach the stoichiometric ratios because of the low chemical equilibrium constant and the low concentration of SO₂.

In this study, we used three common functional ILs ([MEA][Lac], [TMG][Lac], and [N₂₂₂₂][Lac]) mixed with H₂O to prepare the absorbents. After absorbing low-concentration SO₂, the absorbents were regenerated by using H₂S via the Claus reaction. The effect of H₂O on the conversion of absorbed SO₂ was investigated. To explore the mechanism of the Claus reaction in aqueous solutions more intuitively, we took H₂SO₃, NaHSO₃, and Na₂SO₃ as examples to analyze whether the existence of S (IV) would affect the conversion of absorbed SO₂ via the Claus reaction. After giving a supposition, we further explored the influence of existence of S (IV) to clarify the mechanism of the Claus reaction in the presence of water.

2. RESULTS AND DISCUSSION

2.1. Absorption Reaction and Claus Reaction in Three Functional ILs and H₂O Binary Systems. Three functional ILs ([MEA][Lac], [TMG][Lac], and [N₂₂₂₂][Lac]) mixed with H₂O were used as absorbents (m₃H₂O = m₃IL = 1:1). And the absorption capacities of the three absorbents at 40.0 °C are shown in Table 1. It can be seen that the results are consistent with the previous work. For instance, the absorption capacity by [TMG][Lac] is 0.51 mol SO₂/mol IL at a SO₂ concentration of 2% and a water content of 7.3% in simulated flue gas.26 The absorption capacity by [N₂₂₂₂][Lac] is 0.791 mol SO₂/mol IL with 3 vol % SO₂ in flue gas at 60.0 °C.27

According to ref 28, the absorption mechanism of SO₂ in these functional ILs is that SO₂ is absorbed physically and chemically. The physical absorption follows Henry's law. The chemical absorption, taking [N₂₂₂₂][Lac] as an example, follows the reaction as shown in eq 1:29

\[ [\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{Lac}] + \text{SO}_2 \rightleftharpoons [\text{N}_2\text{N}_2\text{N}_2\text{N}_2][\text{Lac}] \cdots \text{SO}_2 \]  

(1)

The conversions of SO₂ absorbed in the three absorbents via the Claus reaction are shown in Table 2. Moreover, we compared the conversion rate of SO₂ in the three systems, and there was a significant decline in an aqueous solution compared with those in pure ILs and EG solutions. However, compared with EG as the solvent, the dissolution phenomenon of sulfur in aqueous absorbents was very low, and the resulted sulfur could be separated easily by centrifugation and filtration. One possible reason might be the very low solubility of sulfur in aqueous solutions, inhibiting the sulfur dissolution in absorbents to a certain extent.

2.2. Effect of Temperature and H₂O Mass Fraction on the Claus Reaction. Taking the [MEA][Lac] aqueous solution as an example, we studied the effect of temperature and H₂O mass fraction on the Claus reaction. The conversions of SO₂ in [MEA][Lac] + H₂O (m₃[MEA][Lac]:m₃H₂O = 1:1) at 40.0, 50.0, and 60.0 °C are shown in Table 3. As can be seen from Table 3, the conversion decreases as the temperature increases, which is consistent with those in ILs and EG binary systems.25 The results demonstrated that the low temperatures would be beneficial to the liquid-phase Claus reaction. This result can satisfy the desired requirement of using the Claus reaction to regenerate functional ILs that is, the temperatures of absorption and regeneration are identical, saving energy.

In our previous work, the mass fraction of EG had no obvious influence on the conversion of SO₂ via the Claus reaction. To investigate whether the content of water has an effect on the conversion, we changed the mass fraction of H₂O in the absorbents to do a series of experiments. Table 4 shows the conversion of SO₂ using the Claus reaction in [MEA][Lac] aqueous solutions with different water contents. According to the results in Table 4, as water contents increased, the conversion decreased. As reported in the literature, the chemical equation of the Claus reaction is shown in eq 2. Therefore, a possible reason might be that the Claus reaction can generate water, and the increase of water content can move the reverse direction of the reversible chemical reaction:

\[ \text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3/8\text{S}_8 + \text{H}_2\text{O} \]  

(2)
and Na2SO3 Aqueous Solutions. The Claus reaction, the three species of S (IV) react with H2S, as H2O; blue circle, 50% [TMG][Lac] + 50% H2O; red triangle, 50% [N2222][Lac] + 50% H2O. (b) Black square, 50% [MEA][Lac] + 50% EG; blue circle, 50% [TMG][Lac] + 50% EG; red triangle, 50% [N2222][Lac] + 50% EG. (b) is adapted with permission from ref25. Copyright 2019 American Chemical Society.

Figure 1. Pressures of H2S as a function of time for the Claus reaction at 40.0 °C in different absorbents. (a) Black square, 50% [MEA][Lac] + 50% H2O; blue circle, 50% [TMG][Lac] + 50% H2O; red triangle, 50% [N2222][Lac] + 50% H2O. (b) Black square, 50% [MEA][Lac] + 50% EG; blue circle, 50% [TMG][Lac] + 50% EG; red triangle, 50% [N2222][Lac] + 50% EG. (b) is adapted with permission from ref 25. Copyright 2019 American Chemical Society.

Table 2. Recovery Ratios of Sulfur in the Three Functional ILs with Different Solvents#*  

| Entry | IL          | R%          | T/°C | P/H2S/MPa | m_IL/m_H2O = 1:1 | m_IL/m_H2O = 1:1 |
|-------|-------------|-------------|------|-----------|------------------|------------------|
| 1     | [MEA][Lac]  | 95.4 ± 1.2  | 40.0 | 1.10      | 96.4 ± 1.1       | 72.4 ± 1.2       |
| 2     | [TMG][Lac]  | 92.5 ± 1.1  | 50.0 | 1.10      | 91.8 ± 1.1       | 85.7 ± 1.1       |
| 3     | [N2222][Lac]| 91.2 ± 1.0  | 60.0 | 1.10      | 90.3 ± 1.2       | 78.7 ± 1.2       |

#The conditions of the Claus reaction: temperature, 40.0 °C; initial pressure of H2S, 1.1 MPa.

Table 3. Recovery Ratios of Sulfur in [MEA][Lac] + H2O (m_MEA/[Lac]=m_H2O = 1:1) at Different Temperatures  

| Entry | IL          | Solvent | T/°C | P/H2S/MPa | R% |
|-------|-------------|---------|------|-----------|----|
| 1     | [MEA][Lac]  | H2O     | 40.0 | 1.10      | 72.4 ± 1.2 |
| 2     | [MEA][Lac]  | H2O     | 50.0 | 1.10      | 70.6 ± 1.1 |
| 3     | [MEA][Lac]  | H2O     | 60.0 | 1.10      | 69.2 ± 1.0 |

Table 4. Recovery Ratios of Sulfur in [MEA][Lac] + H2O with Different Mass Fractions of H2O  

| Entry | IL          | Solvent (mass fraction) | T/°C | P/H2S/MPa | R% |
|-------|-------------|-------------------------|------|-----------|----|
| 1     | [MEA][Lac]  | H2O (25%)               | 40.0 | 1.10      | 86.8 ± 1.1 |
| 2     | [MEA][Lac]  | H2O (50%)               | 40.0 | 1.10      | 72.4 ± 1.2 |

2.3. Study on the Claus Reaction in H2SO3, NaHSO3, and Na2SO3 Aqueous Solutions. In the previous subsections, it can be found that the addition of water can reduce the conversion of SO2 in functional ILs aqueous solution via the Claus reaction. However, water is inevitable in industrial application, and it has a certain influence on the absorption and regeneration stages of functional ILs. As is known, the absorbed SO3 in functional ILs aqueous solution mainly exists as H2SO3, HSO3−, and SO32−. Actually, in the liquid-phase Claus reaction, the three species of S (IV) react with H2S, as shown in eq 3:

\[ \text{H}_2\text{SO}_3 + 2\text{H}_2\text{S} \rightleftharpoons 3/8\text{S}_8 + 3\text{H}_2\text{O} \]  

(3)

To study the effect of water on the Claus reaction, we used H2SO3, NaHSO3, and Na2SO3 aqueous solutions to study the mechanism of the Claus reaction.

The concentration of S (IV) in three aqueous solution is 1.0 mol/L, and the experimental method is the same as that in functional ILs. The conversion was calculated by the ratio of the generated sulfur to the theoretical sulfur. Table 5 shows the conversion of SO3 via the Claus reaction at 40.0 °C. It is very interesting that the conversions have great differences at the same concentrations of S (IV). It should be noted that the conversion is almost zero in the Na2SO3 aqueous solution. We found that the oxidability of three chemical substances varied from pH values of aqueous solutions, and the oxidability order is H2SO3 (SO2) > HSO3− > SO32−, which is in consistence with their standard reduction potentials, 0.45 V, −0.19 V, and −0.90 V, respectively (data were obtained from the refs 31 and 32 and calculated according to the thermodynamics law). The Claus reaction is a redox reaction and the conversion of S (IV) species is directly affected by its oxidability. Therefore, due to its low oxidability, SO32− cannot react with H2S, resulting in its low conversion.

As is known, there is an ionization equilibrium in H2SO3, HSO3−, and SO32− aqueous solution, and the pH of the solution is the determining factor. Table 6 shows the mole fractions of H2SO3, HSO3−, and SO32− at different pH, which were calculated by ionization and hydrolysis equilibrium constant.

As can be seen in Table 6, the mole fraction of H2SO3 decreases as the pH increases or the acidity decreases. When pH value of the aqueous solution is 1, the mole fraction of H2SO3 is 87.0%; when pH value of the aqueous solution is 6 and higher, there is no H2SO3. By the contract, the mole fraction of HSO3− first increases and then decreases as the pH increases or the acidity decreases. The mole fraction of HSO3− is 13.0% at a pH value of 1, and it increases to a maximum value of 99.2% at a pH value of 4 and decreases to 9.1% at a...
**Table 6. Mole Fractions of H$_2$SO$_4$, HSO$_3^-$, and SO$_3^{2-}$ at Different pH in Aqueous Solution at 25 °C**

| pH | $\delta$(H$_2$SO$_4$)/% | $\delta$(HSO$_3^-$)/% | $\delta$(SO$_3^{2-}$)/% |
|----|-------------------------|-------------------------|-------------------------|
| 1  | 87.0                    | 13.0                    | 0                       |
| 2  | 40.0                    | 60.0                    | 0                       |
| 3  | 6.3                     | 93.7                    | 0                       |
| 4  | 0.7                     | 99.2                    | 0.1                     |
| 5  | 0.1                     | 98.9                    | 1.0                     |
| 6  | 0                       | 90.9                    | 9.1                     |
| 7  | 0                       | 50.0                    | 50.0                    |
| 8  | 0                       | 9.1                     | 90.9                    |

“The pH values of aqueous solutions were adjusted by HCl and NaOH. The total concentration of H$_2$SO$_4$, HSO$_3^-$, and SO$_3^{2-}$ is 1 mol/L, and the initial pressure of H$_2$S is 1.1 MPa.

As can be seen in Table 7, the pH values after the reaction are between 7 and 8 no matter the pH value before the Claus reaction. As the pH value before the Claus reaction increases from 2.12 to 7.07, the recovery ratio of sulfur decreases from 49.9% to 0.2%. Two conclusions can be drawn from Table 7. The first one is that the Claus reaction is accompanied by the consumption of H$_2$SO$_4$ and HSO$_3^-$, and then the content of SO$_3^{2-}$ increases after the Claus reaction. Hence, the acidity of the solution decreases as the pH values are between 7.02 and 7.96. The second one is that the stronger the acidity of the solution, the higher the conversion of SO$_2$ via the Claus reaction as the recovery ratio of sulfur is the highest at the lowest pH value of 2.12, which indicates that an acidic aqueous solution is more beneficial to the Claus reaction.

### 2.4. Effect of pH of Absorbents on the Claus Reaction

According to the above results, it can be found that the pH of the aqueous solution can affect the species of S (IV), which can then further affect the conversion rate of the Claus reaction. Whether the conclusions are applicable to the functional ILs, aqueous solution needs further experimental exploration.

First of all, we investigated the effect of the H$_2$SO$_4$ on the pH of [TMG][Lac] aqueous solution ($w_{[TMG][Lac]} = 60\%$), SO$_2$ absorption capacity, and the conversion of SO$_2$ via the Claus reaction. **Table 8** shows the absorption capacity of SO$_2$ (2 vol %) and the conversion of SO$_2$ via the Claus reaction at 40.0 °C. It can be concluded from Table 8 that the conversion increases with the pH value decrease. However, there are two points to which attention should be paid. First, with the increase of H$_2$SO$_4$ content above 2%, the conversion increases to about 91% and remains unchanged. Second, the change of the pH of the absorbents by adding H$_2$SO$_4$ can improve the conversion of SO$_2$ via the Claus reaction but also reduce the absorption capacity of SO$_2$. Therefore, it is necessary to increase the conversion by adding an acid in a proper range.

However, H$_2$SO$_4$ is a kind of inorganic strong acid, and it has some interference to the system; thus, we used lactic acid to adjust the acidity of absorbents. Specifically, the functional ILs were synthesized with different mole ratios of MEA (or TMG) and lactic acid. SO$_2$ absorption capacity and recovery ratios of the Claus reaction in [MEA][Lac] and [TMG][Lac] aqueous solutions with different amounts of added lactic acid are shown in **Table 9** and **Table 10**. The concentration of SO$_2$ was 2 vol %, and the temperatures of SO$_2$ absorption and the Claus reaction were both 40.0 °C.

**Table 7. pH Value of NaHSO$_3$ Aqueous Solution before and after the Claus Reaction and Its Recovery Ratio of Sulfur**

| entry | pH (before the Claus reaction) | pH (after the Claus reaction) | $R_3$/% |
|-------|--------------------------------|------------------------------|--------|
| 1     | 2.12                           | 7.02                         | 49.9 ± 1.0 |
| 2     | 3.52                           | 7.21                         | 37.3 ± 1.2 |
| 3     | 5.05                           | 7.96                         | 34.8 ± 1.1 |
| 4     | 5.95                           | 7.82                         | 19.7 ± 1.0 |
| 5     | 7.07                           | 7.34                         | 0.2 ± 1.1  |

“The conditions of the Claus reaction: the concentration of NaHSO$_3$ 1 mol/L; initial pressure of H$_2$S, 1.1 MPa; the temperature, 40.0 °C.

**Table 8. Effect of Amount of Added H$_2$SO$_4$ on SO$_2$ Absorption and the Claus Reaction in [TMG][Lac] Aqueous Solution**

| $w$ (H$_2$SO$_4$) | pH$_{abs}$ | absorption capacity (g SO$_2$/g abs) | $R_3$/% |
|------------------|------------|--------------------------------------|--------|
| 0                | 8.20       | 0.120                                | 86.1 ± 1.0 |
| 2%               | 5.85       | 0.101                                | 91.2 ± 1.0 |
| 4%               | 5.37       | 0.086                                | 91.4 ± 1.1 |
| 6%               | 5.00       | 0.074                                | 91.2 ± 1.2 |
| 8%               | 4.59       | 0.055                                | 91.6 ± 1.0 |
| 10%              | 4.29       | 0.039                                | 91.1 ± 1.1 |

“The concentration of [TMG][Lac] in aqueous solutions is 60 wt % ($w_{[TMG][Lac]} = 60\%$), the concentration of SO$_2$ is 2 vol %, the temperature of SO$_2$ absorption of is 40 °C, and the temperature of the Claus reaction is 40 °C.

**Table 9. Effect of $n_{HLac}/n_{[MEA][Lac]}$ on SO$_2$ Absorption and the Claus Reaction in [MEA][Lac] Aqueous Solution**

| $n_{HLac}/n_{[MEA][Lac]}$ | absorption capacity (g SO$_2$/g abs) | $R_3$/% |
|---------------------------|--------------------------------------|--------|
| 0:1                       | 0.067                                | 72.4 ± 1.1 |
| 0.1:1                     | 0.053                                | 75.3 ± 1.0 |
| 0.2:1                     | 0.050                                | 77.2 ± 1.2 |
| 0.3:1                     | 0.040                                | 78.0 ± 1.0 |
| 0.4:1                     | 0.035                                | 81.2 ± 1.1 |

“The concentration of [MEA][Lac] in aqueous solutions is 50 wt %, the concentration of SO$_2$ is 2 vol %, the temperature of SO$_2$ absorption is 40 °C, and the temperature of the Claus reaction is 40 °C.

**Table 10. Effect of $n_{HLac}/n_{[TMG][Lac]}$ on SO$_2$ Absorption and the Claus Reaction in [TMG][Lac] Aqueous Solution**

| $n_{HLac}/n_{[TMG][Lac]}$ | absorption capacity (g SO$_2$/g abs) | $R_3$/% |
|---------------------------|--------------------------------------|--------|
| 0:1                       | 0.089                                | 85.7 |
| 0.05:1                    | 0.081                                | 85.7 |
| 0.1:1                     | 0.078                                | 85.7 |
| 0.2:1                     | 0.073                                | 87.3 |
| 0.3:1                     | 0.069                                | 88.1 |

“The concentration of [TMG][Lac] in aqueous solutions is 50 wt %, the concentration of SO$_2$ is 2 vol %, the temperature of SO$_2$ absorption is 40.0 °C, and the temperature of the Claus reaction is 40.0 °C.”
Figure 2. Stoichiometry of [MEA][Lac] absorbing SO₂.

\[
2 \left[ \text{HO-CH}_2\text{-CH}_2\text{-NH}_2 \right] \text{OH} + \text{SO}_2 \rightarrow \left[ \text{HO-CH}_2\text{-CH}_2\text{-NH}_2 \right] \text{OH} + 2 \text{H}_2\text{C-CH-C-OH} + \text{S}_2\text{O}_3^{2-}
\]

Figure 3. Stoichiometry of the Claus reaction in [MEA][Lac] after absorbing SO₂.

Through the exploration of effect of pH on the Claus reaction in functional ILs aqueous solutions, it can be found that the addition of lactic acid increases the conversion of SO₂ via the Claus reaction, but the increase is limited. Moreover, the SO₂ absorption capacity decreases with the addition of lactic acid, but the decrease is not significant compared to the addition of H₂SO₄.

2.5. Stoichiometry of the Claus Reaction in Functional Ionic Liquids Aqueous Solution. Through the above research, it can be found that the stoichiometry of the Claus reaction is different in the presence of water or the no-water case. We suppose that it is mainly due to the different absorption mechanism in the two cases.

Taking [MEA][Lac] as an example, the stoichiometry of SO₃ absorption in absence of water is shown in Figure 2. It is speculated that the Claus reaction mechanism in [MEA][Lac] in the absence of H₂O is shown in Figure 3.33

In the presence of water, the stoichiometry of [MEA][Lac] absorbing SO₂ is shown in eqs 4 and 5:²⁷⁻²⁹

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3
\]

\[
\text{H}_2\text{SO}_3 + [\text{MEA}][\text{Lac}] \rightarrow [\text{MEA}][\text{HSO}_3] + \text{H Lac}
\]

The stoichiometry of the Claus reaction in [MEA][Lac] aqueous solution is shown in eq 6:

\[
\text{HSO}_3^- + 2\text{H}_2\text{S} + \text{H}^+ \rightarrow 3/8\text{S}_8 + 3\text{H}_2\text{O}
\]

It can be seen from the above analysis whether the species of SO₂ after absorption are different in the presence of water or not, which results in a different mechanism of the Claus reaction. In an aqueous solution, the absorbed SO₂ exists in species of H₂SO₃, HSO₃⁻, and SO₃²⁻. There is an equilibrium of ionization and hydrolysis between the three substances, which is mainly affected by pH of the solution. With the consumption of H⁺ during the Claus reaction, the alkalinity of the solution gradually increases, and the absorbed SO₂ mainly exists in SO₃²⁻, which cannot react with H₂S. However, in the absence of water, SO₂ is directly absorbed by ILs to form IL-SO₂. During the Claus reaction, the chemical bond between SO₂ and IL is broken, and the SO₂ reacts with H₂S. In the process, the existing form of SO₂ does not change after being absorbed, and its ability of reacting with H₂S does not decrease. Instead, the pure IL environment provides a unique ionic environment, which has certain catalysis effect on the Claus reaction. Therefore, the presence of water influences not only the reaction rate but also the conversion of SO₂ via the Claus reaction of H₂S with SO₂ absorbed in functional ILs. However, it has been found that the addition of lactic acid increases the conversion of SO₂ via the Claus reaction. This work provides the information on the Claus reaction for the absorbed SO₂ not only by functional ILs but also by functional deep eutectic solvents in the presence of water.

3. CONCLUSIONS

In this work, we mixed water with three functional ILs to yield aqueous absorbents of [MEA][Lac] + H₂O, [TMG][Lac] + H₂O, and [N₂₂₂₂][Lac] + H₂O, and studied the effect of water on the Claus reaction in three absorbents due to the presence of water in flue gas and then in absorbents. The result shows that the addition of water into ILs can reduce the conversion of absorbed SO₂, and the conversion increases as the acidity of absorbents increases. To explain this phenomenon, the Claus reaction was performed in H₂SO₄, NaHSO₃, and Na₂SO₃ aqueous solutions. It turns out that the conversion of SO₂ via the Claus reaction is related to the species of S (IV), the conversion rate, H₂SO₃ > H₂SO₄ > SO₃²⁻, and their proportions dependent on the pH of solutions. On the basis of the absorption mechanism of SO₂ in functional ILs aqueous solution, H₂S reacts with HSO₃⁻ and SO₃²⁻ with weaker oxidability, resulting in the lower conversion rate.

4. EXPERIMENTAL SECTION

4.1. Materials. SO₂ (99.95%), H₂S (99.95%), and N₂ (99.99%) were obtained from Beijing Beijin Gases Co., Ltd. (Beijing, China). Simulated flue gas with SO₂ (2%) was prepared by mixing SO₂ and N₂ in a 40 dm³ high-pressure cylinder. Analytical reagent 1,1,3,3-tetramethylguanidine (99%), tetraethylammonium hydroxide (25% in water), ethylene glycol (EG), and lactic acid (85%–90% in water) were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Monoethanolamine (99%) was purchased from Alfa Aesar (China) Chemicals Co., Ltd. (Beijing, China). NaOH (97%), H₂SO₃, NaHSO₃, and Na₂SO₃ were purchased from Beijing Chemical Works (Beijing, China). All reactants and solvents were A.R. grade.

[MEA][Lac],[TMG][Lac], and [N₂₂₂₂][Lac] with different mass fractions of water or EG were synthesized and characterized following the literature.³⁴ The water contents in the absorbents were determined by Karl Fischer titration (Leici ZDY-502, China).

4.2. Absorption of Low-Concentration SO₂ in Absorbents. The schematic diagram of the apparatus is shown in Figure 4. The simulated flue gas with 2% SO₂ with a flow of 100 cm³/min was bubbled through water and absorbents successively to offset the reduction of water contents of absorbents. The concentrations of SO₂ in absorbents were analyzed using an iodine titration method (HJT 56–2000, a standard method of the State Environmental Protection Administration of China). After a period of absorption, the concentration of SO₂ no longer changed, meaning that the absorbents were saturated.

4.3. Regeneration of Absorbents via the Claus Reaction. The regeneration method was the same as that reported in the literature.²⁵ Briefly, the regeneration reaction was carried out in a stainless-steel chamber (25.641 dm³).
Figure 4. Schematic diagram of the apparatus for ILs to absorb SO₂ from a flue gas stream. 1. Simulated flue gas cylinder; 2. pressure reducing value; 3. rotameter; 4. glass tube with H₂O; 5. glass tube with absorbents; 6. tail gas absorption device; 7. water bath.

equipped with a temperature sensor (±0.1 °C), a pressure sensor (±0.01 MPa), and a magnetic stirrer. A sample of SO₂-absorbed functional IL with or without water was loaded in the drying. Because of the physical absorption of H₂S, the residual pure sulfur was obtained by centrifugation, washing, and then the Claus reaction was started. The pressure in the chamber was recorded at certain time intervals until the pressure remained constant, indicating that the reaction reached its equilibrium.

The conversion of SO₂ in the Claus reaction was calculated via the recovery ratio of sulfur (Rₙ). After the Claus reaction, pure sulfur was obtained by centrifugation, washing, and drying. Because of the physical absorption of H₂S, the residual H₂S in the regenerated absorbents was easily removed by a decompression method, and then it could be used for SO₂ absorption.

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Notes

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