The CO₂ Absorption in Flue Gas Using Mixed Ionic Liquids

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Abstract: Because of the appealing properties, ionic liquids (ILs) are believed to be promising alternatives for the CO₂ absorption in the flue gas. Several ILs, such as [NH₃emim][BF₄], [C₄mim][OAc], and [NH₃emim][OAc], have been used to capture CO₂ of the simulated flue gas in this work. The structural changes of the ILs before and after absorption were also investigated by quantum chemical methods, FTIR, and NMR technologies. However, the experimental results and theoretical calculation showed that the flue gas component SO₂ would significantly weaken the CO₂ absorption performance of the ILs. SO₂ was more likely to react with the active sites of the ILs than CO₂. To improve the absorption capacity, the ionic liquid (IL) mixture [C₄mim][OAc]/[NH₃emim][BF₄] were employed for the CO₂ absorption of the flue gas. It is found that the CO₂ absorption capacity would be increased by about 25%, even in the presence of SO₂. The calculation results suggested that CO₂ could not compete with SO₂ for reacting with the IL during the absorption process. Nevertheless, SO₂ might be first captured by the [NH₃emim][BF₄] of the IL mixture, and then the [C₄mim][OAc] ionic liquid could absorb more CO₂ without the interference of SO₂.

Keywords: flue gas; carbon dioxide; absorption; ionic liquids

1. Introduction

The CO₂ absorption of flue gas is an important process for reducing greenhouse gas [1]. To date, most flue absorptions are performed by using amine solvents. However, conventional absorption methods usually have some disadvantages: High equipment corrosion rate, high absorbent make-up rate due to the amine degradation by SO₂, NO₂, and O₃ in the flue gas, and high energy consumption during the regeneration process [2]. In the last decades, ionic liquids (ILs) have been used in many fields. Multifunctional ionic liquids are easily prepared, and the vapor pressure of ionic liquids can be neglected [3]. The other attractive properties of ILs include: High thermal stability, large electrochemical window, and high dissolve ability of compounds [4]. Blanchard et al. [5] have reported that certain ILs can considerably dissolve CO₂ gas. Since then, ILs for CO₂ capture have attracted much attention. For example, multi-N-containing ionic liquids can absorb much more SO₂/CO₂ in the flue gas than that of the limestone solvent [6]. Shiflett et al. [7,8] have found that the imidazolium-based ionic liquid [C₄mim][OAc] can markedly reduce the energy losses of CO₂ absorption comparing with those of the commercial monoethanolamine solvent. Guanidinium salt ILs (e.g., [TMG][L]) and functional ILs (e.g., [NH₃p-bmim][BF₄] and 2-(2-hydroxyethoxy) ammonium acetate) all show high efficiency for CO₂ and SO₂ capture [9,10].

The typical flue gas from coal-burning usually contains about 15 vol% CO₂, 10 vol% H₂O, and more than 2 vol% SO₂ [11]. Apart from CO₂, the effects of SO₂ on the flue gas absorption should be
taken into account [12]. Most researchers consider that water has a little influence on the CO$_2$ capture, but the effects of SO$_2$ would not be neglected. For the impurities of the flue gas, it is found that the ILs are more likely to absorb SO$_2$ than CO$_2$. Specifically, the N element of the ionic liquid (IL) prefers to capture the SO$_2$ molecules, and then CO$_2$ molecules are repelled by the captured SO$_2$ [13]. Thus, the CO$_2$ absorption capacity of ionic liquids would be rapidly decreased over several cycles. Moreover, almost all of the ILs would exhibit much higher SO$_2$ absorption capacity than CO$_2$ due to the higher solubility of SO$_2$ in ILs. For instance, pure CO$_2$ solubility in the guanidinium-based ILs was only 0.4 mol/mol, while the SO$_2$ solubility in these ILs was as high as 2.5 mol/mol under the same conditions [10]. For an extreme case, the absorption capacities of pure SO$_2$ and CO$_2$ in the azole-based ILs (e.g., [P$_66614$][Im]) were 3.5 mol/mol and 0.1 mol/mol, respectively [14]. Although SO$_2$ has stronger interactions with ILs than CO$_2$ does, the actual partial pressure of SO$_2$ in the flue gas is very low [15]. It is well accepted that the partial pressure of SO$_2$ is about two orders of magnitude lower than that of CO$_2$, and low SO$_2$ partial pressure usually leads to low absorption capacity for SO$_2$. That is, a lot of energy will be consumed to remove SO$_2$ and CO$_2$ from the flue gas, if we used a two-step absorption process (absorbing SO$_2$ at first, and then CO$_2$).

The effects of single IL on the CO$_2$ capture have been widely discussed in recent years [2,7,16-19]. However, there are few reports on the IL mixtures for CO$_2$ absorption, especially on the CO$_2$ capture from the flue gas. Therefore, if the IL mixture was employed, the CO$_2$ absorption capacity of the mixed ILs might be greater than that of the single ionic liquid. Specifically, if the SO$_2$ of flue gas was absorbed by one IL of the mixture, the negative influence of SO$_2$ on the whole IL mixture might be significantly decreased, and then more CO$_2$ could be captured.

In this work, we want to use IL mixtures to remove CO$_2$ and SO$_2$ from the flue gas. The amine-functional ionic liquid [NH$_2$emim][BF$_4$] and the imidazolium-based ionic liquid [C$_4$mim][OAc] were synthesized at first. Subsequently, the two ILs were mixed to investigate the CO$_2$ and SO$_2$ absorption. Here, [NH$_2$emim][BF$_4$] was mainly used to absorb SO$_2$ in the flue gas, while the [C$_4$mim][OAc] ionic liquid was employed to capture CO$_2$. In order to more clearly study the actual flue gas, the CO$_2$ absorption performance in the IL mixture was measured at the simulated flue gas with 15 vol% CO$_2$ and 2 vol% SO$_2$. The effect of SO$_2$ on the IL mixture and the interaction between CO$_2$ and SO$_2$ in the IL absorption were also studied. Furthermore, the absorption mechanism at the molecule level was investigated by the quantum chemical calculation and the instrumental analysis.

2. Results and Discussion

2.1. CO$_2$ and SO$_2$ Absorption Performance of the Single ILs

When the simulated flue gas (15% CO$_2$/85% N$_2$) only contains the CO$_2$ impurity, one mole [C$_4$mim][OAc] could absorb 0.298 mol CO$_2$ (Table 1). However, when SO$_2$ was mixed in the simulated flue gas (15% CO$_2$/2% SO$_2$/N$_2$), the CO$_2$ absorption capacity of [C$_4$mim][OAc] was reduced to 0.204 CO$_2$/mol IL. The result shows that SO$_2$ has a negative effect on the IL absorbing CO$_2$. The single IL [NH$_2$emim][OAc] and [NH$_2$emim][BF$_4$] were also used to capture the CO$_2$ of flue gas. Without the interference of SO$_2$, the CO$_2$ absorption capacities of [NH$_2$emim][OAc] and [NH$_2$emim][BF$_4$] were 0.291 mol CO$_2$/mol IL and 0.290 mol CO$_2$/mol IL, respectively. However, like the [C$_4$mim][OAc] ionic liquid, the CO$_2$ absorption capacities under exposure to 2% SO$_2$ would be markedly decreased to 0.171 mol CO$_2$/mol [NH$_2$emim][OAc] and 0.180 mol CO$_2$/mol [NH$_2$emim][BF$_4$], respectively. In short, the single ionic liquids all exhibit the CO$_2$ absorption capacities, but this capacity would be greatly weakened by the interference of SO$_2$. 


Table 1. Summary of CO2 absorption capacity by single ionic liquids.

| Ionic Liquids     | T, K | Gas      | Absorption Capacity, mol CO2/mol IL |
|-------------------|------|----------|-------------------------------------|
| [C4mim][OAc]     | 293  | 15% CO2/85% N2 | 0.298                               |
| [C4mim][OAc]     | 293  | 15% CO2/2% SO2/83% N2 | 0.204                               |
| [NH2emim][BF4]   | 293  | 15% CO2/85% N2 | 0.290                               |
| [NH2emim][BF4]   | 293  | 15% CO2/2% SO2/83% N2 | 0.180                               |
| [NH2emim][OAc]   | 293  | 15% CO2/85% N2 | 0.291                               |
| [NH2emim][OAc]   | 293  | 15% CO2/2% SO2/83% N2 | 0.171                               |

The researchers believed that CO2 and SO2 of the flue gas would be absorbed simultaneously [13,20]. The [C4mim][OAc] and [NH2emim][BF4] absorption results supported this conclusion. For example, an experiment was carried out of outlet SO2 concentration vs. time to investigate the SO2 absorption performance. In this study (Figure 1a), the simulated flue gas contained 15% CO2, 2% SO2, and 83% N2. The concentrations of CO2 and SO2 of the outlet stream were simultaneously detected with time. It was found that [C4mim][OAc] and [NH2emim][BF4] all can capture CO2, but the outlet SO2 concentration was hardly detected before 40 min (Figure 1a). It indicates that SO2 could be completely absorbed by [C4mim][OAc] and [NH2emim][BF4] during the absorption process. Additionally, an extreme case was investigated in which the simulated flue gas contained 80% CO2, 2% SO2, and 18% N2. However, SO2 was also not found at the gas stream of the outlet before 15 min. Compared with CO2, SO2 has higher dipole moments and molecular polarity, which often results in the strong affinity of SO2 with ionic liquids [21,22].

![Figure 1](image-url)

**Figure 1.** SO2 absorption performance of [C4mim][OAc] and [NH2emim][BF4]: (a) Outlet SO2 concentration vs. time at the atmosphere of 15% CO2, 2% SO2, and 83% N2; (b) SO2 absorption capacity at the atmosphere of 2% SO2/98% N2.

The presence of SO2 in flue gas usually leads to a competitive and negative influence on the separation of CO2. Figure 2 shows the CO2 absorption performance of [C4mim][OAc] at the atmosphere of 15% CO2/85% N2 and 15% CO2/2% SO2/83% N2, respectively. After 6 regeneration cycles, 1 mol [C4mim][OAc] could absorb 0.255 mol CO2, although the IL absorption capacity slightly decreased. In contrast, the absorption capacity of 1 mol [C4mim][OAc] was only 0.10 mol CO2 after the same number of cycles. In addition, the net SO2 absorption experiment (2% SO2/98% N2) showed that [NH2emim][BF4] has high SO2 absorption capacity (0.35 mol SO2/mol IL), while 1 mol [C4mim][OAc] only absorbs 0.18 mol SO2 (Figure 1b). These results agreed well with previous studies [23–25].

FT-IR can investigate the interaction between IL and CO2/SO2 [26]. The spectra of [C4mim][OAc] showed the changes after 15% CO2 and 2% SO2 absorption, respectively (Figure 3a–c). However, the [C4mim][OAc] spectrum had minimal changes when it was used to remove pure CO2. Although the appearance of the carbonyl band at 1720 cm−1 shows that the acetate anion might be partly converted into the acetate acid [27], Shiflett considered that the amount of such a chemical reaction was minor and reversible [24]. Thus, the other reactions between CO2 and the cation species in this work might...
not be detected within the wavenumber of 800–1600 cm⁻¹, as Figure 3a,c shown. Similarly, the FT-IR spectra of [NH₃emim][BF₄] almost have no change before and after CO₂ absorption (Figure 3d,f), indicating that the chemical reaction between the [NH₃emim] cation and CO₂ was not enough to be detected by FT-IR.

In contrast, the chemical reaction between SO₂ and [C4mim][OAc] was much stronger than that of [C4mim][OAc]–CO₂. Even if there was only a small amount of SO₂ (2%) in the flue gas, the FT-IR spectrum still shows marked changes (Figure 3b). Compared with the spectrum of fresh [C4mim][OAc], the peak intensity at 1580 and 1371 cm⁻¹ decreased significantly as the [C4mim][OAc] absorbing SO₂. Meanwhile, the peaks at 1720, 1321, 1254, 1144, and 950 cm⁻¹ newly appeared in the spectrum. The bands at 1321 and 1144 cm⁻¹ can be attributed to the stretching of SO₂ absorbed by the ionic liquid [26]. After SO₂ absorption, the new peak at 1720 cm⁻¹ shows the formation of a carbonyl group, which also indicates that most of the acetate ions were no longer associated with [C4mim] cations. The intense band at 950 cm⁻¹ should be assigned to the vibrational mode of SO₂⁻ or SO₃²⁻. It once again suggests that the interaction between the SO₂ and [C4mim][OAc] ionic liquid was strong. Similarly, the peak intensity at 885 and 1543 cm⁻¹ changed markedly when the [NH₃emim][BF₄] absorbed SO₂. Particularly, two new peaks appeared at 968 and 1367 cm⁻¹, which can be attributed to the interaction between the N elements of the IL and SO₂ [6].

![Figure 2](image2.png)

**Figure 2.** CO₂ absorption capacity of [C4mim][OAc] during 6 regeneration cycles at the atmosphere of 15% CO₂/85% N₂ and 15% CO₂/2% SO₂/83% N₂.

![Figure 3](image3.png)

**Figure 3.** FT-IR spectra of ionic liquids (ILs): (a) Fresh [C4mim][OAc]; (b) [C4mim][OAc] after SO₂ absorption (2% SO₂/98% N₂); (c) [C4mim][OAc] after CO₂ absorption (15% CO₂/85% N₂); (d) Fresh [NH₃emim][BF₄]; (e) [NH₃emim][BF₄] after SO₂ absorption (2% SO₂/98% N₂); (f) [NH₃emim][BF₄] after CO₂ absorption (15% CO₂/85% N₂).
2.2. CO$_2$/SO$_2$: Absorption Properties in IL Mixtures

Due to the influence of SO$_2$, the CO$_2$ absorption capacity of single ionic liquids was greatly decreased. If [NH$_2$emim][BF$_4$] and [C$_4$mim][OAc] were simultaneously utilized, more CO$_2$ (with SO$_2$) in the flue gas might be captured. The CO$_2$ absorption capacities of IL mixtures at different mole fractions of [C$_4$mim][OAc] or [NH$_2$emim][BF$_4$] were displayed in Figure 4. Here, $X$ is defined as the molar ratio of [NH$_2$emim][BF$_4$] to the IL mixture ([C$_4$mim][OAc]/[NH$_2$emim][BF$_4$]). Compared with the CO$_2$ absorption capacity of the single IL, the IL mixture could remove more CO$_2$. This result may be due to the presence of [NH$_2$emim][BF$_4$]. The small amount of SO$_2$ might be absorbed by [NH$_2$emim][BF$_4$] at first. Without the interference of SO$_2$, the CO$_2$ absorption capacity of the IL mixture was significantly enhanced. It was also found that the absorption of CO$_2$ did not increase significantly with the increase of the $X$ value. When $X$ was 0.3, the CO$_2$ absorption capacity of the [C$_4$mim][OAc]/[NH$_2$emim][BF$_4$] mixture reached up to the maximum. Similarly, when the IL mixture [C$_4$mim][OAc]/[NH$_2$emim][OAc] was used to remove CO$_2$/SO$_2$ of the flue gas, the poison effect of SO$_2$ on [C$_4$mim][OAc] was also greatly reduced. As Figure 4 shows, the CO$_2$ absorption of [C$_4$mim][OAc]/[NH$_2$emim][OAc] was about 0.4 mol CO$_2$/mol IL. Compared to the single [C$_4$mim][OAc], the absorption capacity of the IL mixture was improved.

![Figure 4. CO$_2$: absorption capacity of ionic liquid (IL) mixtures at different $X$: Flue atmosphere 15% CO$_2$/2% SO$_2$/83% N$_2$; absorption temperature, 293 K.](image)

The $^1$H NMR spectrum (Figure 5) shows that SO$_2$ would interact with [NH$_2$emim][BF$_4$] and [NH$_2$emim][OAc]. The NMR data of fresh [NH$_2$emim][BF$_4$] and fresh [NH$_2$emim][OAc] are listed as follows:

Fresh [NH$_2$emim][BF$_4$], $\delta$ = 7.721 (s, 1H, unsaturated C–H in the imidazole ring, with N connected to the left and right), 7.641 (d, 1H, unsaturated C–H in the imidazole ring), 7.636 (d, 1H, unsaturated C–H in the imidazole ring), 4.295 (s, 3H, H$_3$C–N ring), 4.039 (t, 2H, H$_3$C–N ring), 3.112 (m, 2H, N–CH$_2$–C–N ring), and 1.878 (t, 2H, NH$_3$).

Fresh [NH$_2$emim][OAc], $\delta$ = 12.751 (s, 1H, unsaturated C–H in the imidazole ring, with N connected to the left and right), 7.865 (d, 1H, unsaturated C–H in the imidazole ring), 7.703 (d, 1H, unsaturated C–H in the imidazole ring), 3.577 (s, 3H, H$_3$C–N ring), 3.749 (t, 2H, H$_3$C–N ring), 2.693 (m, 2H, N–CH$_2$–C–N ring), 1.973 (t, 2H, NH$_2$) and 1.651 (s, 3H, CH$_3$ in OAc–).

In comparison to the $^1$H NMR spectrum of the fresh [NH$_2$emim][BF$_4$] (Figure 5a), new resonance peaks at 8.10 ppm were found after SO$_2$: absorption, which indicates the formation of S–N [28]. According to this result, it was considered that the interaction between SO$_2$: and [NH$_2$emim][BF$_4$] should mainly occur at the N element of the [NH$_2$emim] cation. For the case of the [NH$_2$emim][OAc] (Figure 5b), a typical peak of –COOH in the $^1$H NMR spectrum moved from 12.75 to 11.83 ppm, and a new resonance peak was observed at 7.52 ppm after SO$_2$: absorption. These results suggest that the interaction between [NH$_2$emim][OAc] and SO$_2$: had occurred [25]. That is, the interaction between
[OAc] and SO2 leads to the moving from 12.75 ppm to 11.83, while the reaction of [NH2emim] and SO2 makes the new peak 7.52 ppm appearance.

In order to further investigate the effects of SO2 on the CO2 absorption capacity of ionic liquids, the CO2 absorption performance of fresh IL and after SO2-saturated IL are illustrated in Figure 6. Specifically, fresh [Cmmim][OAc] and fresh [NH2emim][BF4] ionic liquids were used to absorb SO2 at first. When the IL was saturated by SO2, the CO2 absorption performance of the IL was investigated. It was found that the SO2-saturated [Cmmim][OAc] did not have the ability to absorb CO2. The concentration of CO2 at the outlet was almost equal to that at the inlet. While fresh [Cmmim][OAc] can absorb CO2 even after 60 min. The similar results were also observed using fresh [C2mmim][OAc] and SO2-saturated [C2mmim][OAc] to absorb CO2 [24]. Shiflet et al. considered that the interaction between the [OAc] anion and CO2 plays an important role in the CO2 removal of [OAc]-based ionic liquids [8]. However, the presence of SO2 makes a great impact on the CO2 absorption of [Cmmim][OAc]. In contrast, when [NH2emim][BF4] was saturated by SO2, the [NH2emim][BF4] still had the CO2 absorption capacity. As Figure 6b shows, SO2-saturated [NH2emim][BF4] could capture about 2–7% CO2 during the absorption process.

![Figure 5. 1H NMR spectra of ILs: (a) [NH2emim][BF4]; (b) [NH2emim][OAc].](image)

![Figure 6. CO2 absorption performance of fresh IL and after SO2 saturated IL: (a) [Cmmim][OAc]; (b) [NH2emim][BF4].](image)

2.3. Quantum Chemical Calculation on the Interaction of IL Mixture with CO2/SO2

The absorption capacity of CO2 in the IL mixtures was higher than that of the single ionic liquid. This may be related to the interactions between ILs and CO2/SO2 molecules. Thus, the interaction of the [Cmmim][OAc] anion and [NH2emim][BF4] with CO2/SO2 was deeply investigated through quantum chemical calculation, which might be helpful to understand well the roles of CO2 and SO2 in the IL absorption. In this work, the structure of [NH2emim][BF4] and [Cmmim][OAc] was optimized on the basis of DFT-D3 calculation at first. The configuration of the IL with the lowest energy was considered as the optimized structure. Additionally, the structures of [Cmmim][OAc] and...
[NH₃emim][BF₄] with CO₂ and SO₂ were also investigated (Figure 7). The structural parameters for the IL–CO₂/SO₂ complexes are listed in Table 2.

![Optimized structure of the complexes of IL with CO₂/SO₂](image)

**Figure 7.** Optimized structure of the complexes of IL with CO₂/SO₂: (a) [NH₃emim][BF₄]–SO₂; (b) [NH₃emim][BF₄]–CO₂; (c) [C₄mim][OAc]–SO₂; (d) [C₄mim][OAc]–CO₂.

**Table 2.** Structural parameters for the complexes.

| Structural Parameters       | CO₂–[NH₃emim][BF₄] | SO₂–[NH₃emim][BF₄] | [C₄mim][OAc]–CO₂ | [C₄mim][OAc]–SO₂ |
|-----------------------------|---------------------|---------------------|-------------------|-------------------|
| C–O, Å                      | 1.19                | 1.21                |                   |                   |
| ∠O–C–O, °                   | 112°                | 112°                |                   |                   |
| S–O, Å                      | 1.46                | 1.49                |                   |                   |
| ∠O–S–O, °                   | 113.5°              | 112.6°              |                   |                   |

In general, the CO₂/SO₂ gas molecules around the anions and cations were related to the absorption reaction. As Figure 7a shows, there was a strong interaction between the N atom and the S atom of SO₂. Due to the complexation of SO₂–N, the average angle of SO₂ was 116.0°. Compared to 119.5° of the pure SO₂ molecule, the bending degree of O=S=O was increased. Similarly, [NH₃emim][BF₄] also leads to an impact on the CO₂ structure. The angle of CO₂ was bent from 180° to 166°, and the bond length of C–O was extended from 1.16 Å to 1.19 Å. For the cases of [C₄mim][OAc], the interaction between the O and the C atom of carbon dioxide was also strong due to the negatively charged oxygen (O atom) in the [OAc] anion. The curvature of CO₂ could be increased by the interaction of the [OAc] anion. The average angle of CO₂ was bent to 146°, and the bond length of C–O was elongated to 1.21 Å. The configurations in Figure 7 also suggest that [NH₃emim] cation and [OAc] anion are the active sites for CO₂/SO₂ absorption.

To some extent, the interaction energy and absorption enthalpy might reflect the absorption capacity of the ILs. It was found that the NH₃emim] cation and [OAc] anion were the main active sites for the absorption of CO₂ and SO₂. In order to save the calculation cost and reduce the interference of other ions, herein, only the thermodynamic data of [OAc]–CO₂, [OAc]–SO₂, CO₂–[NH₃emim], and SO₂–[NH₃emim] complexes were compared (Table 3). It was found that the interaction energy and absorption enthalpy of [OAc]–CO₂–SO₂ complex were less than the sum of the energy and the enthalpy for [OAc]–CO₂ and [OAc]–SO₂, suggesting that CO₂ and SO₂ would competitively react with [OAc] anion.

In contrast, the interaction energy and absorption enthalpy of [NH₃emim]–CO₂–SO₂ complex were approximately equal to the sum of those for the [NH₃emim]–CO₂ and [NH₃emim]–SO₂ complexes, indicating that the competitive reaction between [NH₃emim]–CO₂ and [NH₃emim]–SO₂ was not obvious. The absorption reaction might also lead to a change in charge distribution. It was
found that the amount of net charge transfer from CO$_2$ to [NH$_2$emim] in [NH$_2$emim]-CO$_2$-SO$_2$ complex was almost equal to that of [NH$_2$emim]-CO$_2$, suggesting that [NH$_2$emim] had strong interactions with either SO$_2$ or CO$_2$. However, due to the impact of SO$_2$, the net charge transfer from [OAc] to CO$_2$ was significantly reduced from −0.510 in the [OAc]-CO$_2$ complex to −0.035 in [OAc]-CO$_2$-SO$_2$ complex, respectively, which might account for the decrease of CO$_2$ absorption capacity for [Cmim][OAc] in Table 1.

**Table 3.** Thermochemical parameters and charge transfer of the ion-CO$_2$/SO$_2$ complexes.

|                  | OAc-CO$_2$ | OAc-SO$_2$ | OAc-CO$_2$-SO$_2$ |
|------------------|------------|------------|-------------------|
| ΔE, kJ/mol       | −40.7      | −113.4     | −140.0            |
| ΔH, kJ/mol       | −46.5      | −125.1     | −151.4            |
| ΔG, kJ/mol       | −1.6       | −70.8      | −72.1             |
| net charge transfer, e | −0.510    | −0.382     | −0.035(CO$_2$)/−0.316(SO$_2$) |

|                  | CO$_2$-[NH$_2$emim] | SO$_2$-[NH$_2$emim] | SO$_2$-[NH$_2$emim] |
|------------------|----------------------|----------------------|----------------------|
| ΔE, kJ/mol       | −33.8                | −123.9               | −156.8               |
| ΔH, kJ/mol       | −36.3                | −126.7               | −160.1               |
| ΔG, kJ/mol       | −7.2                 | −55.1                | −61.9                |
| net charge transfer, e | −0.312              | −0.399               | −0.308(CO$_2$)/−0.334(SO$_2$) |

Table 4 collects the thermochemical data of [NH$_2$emim][BF$_4$]-CO$_2$ and [NH$_2$emim][BF$_4$]-SO$_2$ complexes. In order to consider the solvent effect of ionic liquids, the continuum universal solvation model (SMD) was used in the calculation. Based on the SMD model, the interaction energies of [NH$_2$emim][BF$_4$]-CO$_2$ and [NH$_2$emim][BF$_4$]-SO$_2$ system were −16.8 and −76.3 kJ/mol, respectively. They were lower than those in the gas phase (−19.2 and −85.4 kJ/mol). Notably, the difference between the interaction energy ([NH$_2$emim][BF$_4$]-CO$_2$ and [NH$_2$emim][BF$_4$]-SO$_2$) in the gas phase (59.5 kJ/mol) was very consistent with the energy difference (66.2 kJ/mol) using the SMD model. In the liquid phase, the interaction energy between [NH$_2$emim][BF$_4$] and SO$_2$ was slightly greater than that of [NH$_2$emim][BF$_4$]-CO$_2$, suggesting that [NH$_2$emim][BF$_4$] tends to react with SO$_2$ rather than with CO$_2$ during the absorption process. Similarly, this phenomenon could also be observed in the thermodynamic data of the [Cmim][OAc]-CO$_2$ and [Cmim][OAc]-SO$_2$ complexes. In short, SO$_2$ was more active than CO$_2$ in the reaction with ionic liquids, and the [NH$_2$emim][BF$_4$] may be more likely to absorb SO$_2$.

**Table 4.** Thermochemical parameters for the IL-CO$_2$/SO$_2$ complexes*.

|                  | [Cmim][OAc]-CO$_2$ | [Cmim][OAc]-SO$_2$ | CO$_2$-[NH$_2$emim][BF$_4$] | SO$_2$-[NH$_2$emim][BF$_4$] |
|------------------|--------------------|--------------------|-----------------------------|-----------------------------|
| ΔE, kJ/mol       | −26.4 (−21.9)      | −80.1 (−70.5)      | −19.2 (−16.8)               | −85.4 (−76.3)               |
| ΔH, kJ/mol       | −30.5              | −93.2              | −29.1                       | −91.5                       |
| ΔG, kJ/mol       | −2.7               | −40.6              | 8.1                         | −37.2                       |

* Values of brackets were calculated by the continuum universal solvation model (SMD).

The interaction between IL mixture ([Cmim][OAc][NH$_2$emim][BF$_4$]) and CO$_2$/SO$_2$ has also been investigated by the quantum chemistry calculation. The optimized structure is displayed in Figure 8. In the mixed ionic liquids, it is found that SO$_2$ was close to [NH$_2$emim][BF$_4$], while the CO$_2$ molecule was near the [Cmim][OAc] ionic liquid. Specifically, SO$_2$ would have interacted with the N atom on the [NH$_2$emim] cation, and CO$_2$ was more likely to react with the [OAc] anion. This result might explain why the IL mixture can more effectively absorb the CO$_2$ of flue gas. Because of the existence of [NH$_2$emim][BF$_4$], SO$_2$ may be first captured by [NH$_2$emim]. Without the interference of SO$_2$, the [Cmim][OAc] ionic liquid then could absorb more CO$_2$. 
3. Materials and Methods

3.1. Materials

The simulated flue gas was obtained by pure gas CO₂, SO₂, and N₂ (purity of >99.99 wt%). They were all purchased from Beifen (China) Gas Technology Company. 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]), 99 wt% was obtained from Sigma-Aldrich Chemical Co., but the ionic liquid 1-butyl-3-methylimidazolium acetate ([C₄mim][OAc]), 99 wt% were purchased from Lanzhou Greenchem ILs, LiCP, CAS, China. Additionally, [NH₄emim][BF₄] and [NH₄emim][OAc] have been synthesized by ourselves in this work. The used materials were as follows: 1-methylimidazole (C₄H₆N₂), 2-bromoethylamine hydrobromide (C₄H₇Br₂N), sodium acetate anhydrous (CH₃COONa), 1-methylimidazole (C₄H₆N₂), acetic acid (CH₃COOH), and sodium borate (NaBF₄). They were all provided by Sinopharm Chemical Reagent Co., Ltd., China, with purity over 98 wt%.

3.2. Ionic Liquid Preparation

In this work, the ionic liquids [NH₄emim][BF₄] and [NH₄emim][OAc] were prepared by ourselves according to the method [17,18,29]. First, the [NH₄emim] cation was prepared by the reaction of 1-methylimidazole and 2-bromoethylamine hydrobromide under reflux for 12 h. Second, the [NH₄emim]-based IL was simply synthesized by ion exchange with NaBF₄ or NaOAc/CH₃COOH in ethanol, and then the ethanol was removed in vacuum. The structures of the ILs were confirmed by proton nuclear magnetic resonance (¹H NMR, Bruker WB400 AMX spectrometer, Billerica, MA, USA). Here, deuterated chloroform (CDCl₃) was used as a solvent, and tetramethylsilane (TMS) was employed as an internal standard for ¹H NMR measurement.

3.3. CO₂ and SO₂ Absorption

As Figure 9 shows, CO₂ and SO₂ absorption experiments were performed in a 30 mL reactor immersed with a water-bath temperature controller. The temperatures were controlled at 293 K for absorption and 353 K for desorption, respectively. The simulated flue gas was a mixture of N₂, CO₂, and SO₂ in accordance with a certain proportion. As a typical absorption process, 10 mL IL or IL mixtures were added to the reactor at first. Subsequently, 15 vol% CO₂, 2 vol% SO₂, and 83 vol% N₂ were mixed in storage. The intake speed of the mixed gas was controlled at 60 mL/min, and the absorption pressure was controlled at 101.3 kPa. The concentrations of CO₂ and SO₂ were analyzed by a gas analyzer (MRU NOVA2000) at the outlet. To investigate the IL regeneration, CO₂ or SO₂ saturated IL was also loaded in the reactor. Desorption was performed at 353 K under a pure N₂ gas atmosphere for 30 min.
The amount of absorbed CO₂ or SO₂ was calculated by the following equation.

\[ A_{\text{gas}} = \frac{M_{\text{IL}} \rho_{\text{gas}} \int_{t_1}^{t_2} (C_0 - C_{\text{gas}}(t)) \, dt}{m_{\text{IL}} M_{\text{gas}}} \]

where \( A_{\text{gas}} \) is the molar amount of CO₂ or SO₂ in the ionic liquid; \( Q \) is the flow rate of the gas stream; \( C_0 \) and \( C_{\text{gas}} \) are the CO₂ or SO₂ concentrations at the inlet and the outlet streams, respectively; \( t_1 \) refers to the beginning time of the absorption process; when the CO₂ and SO₂ concentrations at the outlet stream returns to the initial concentration, the time is \( t_2 \); \( M_{\text{IL}} \) and \( M_{\text{gas}} \) are the molecular weight of IL and CO₂ (or SO₂), respectively; \( m_{\text{IL}} \) is the weight of the ILs, and \( \rho_{\text{gas}} \) is the density of CO₂ or SO₂.

After the IL was saturated by CO₂ and SO₂, the complex structure was investigated by the FTIR and NMR technologies. The FTIR spectra of the samples were analyzed on an FTIR spectrometer (PerkinElmer, Frontier 2500). In addition, the structure changes of the [NH₃emim]-based IL after absorption were also detected by the NMR spectrometer (Bruker WB400 AMX, 300 MHz) using chloroform-d (CDCl₃) as a solvent and tetramethylsilane (TMS) as an internal standard.

3.4. Theoretical Calculation

A quantum chemical calculation was used in this work to study the interaction between the ionic liquid and CO₂ with SO₂. All calculations were carried out by the Gaussian 16 program [30]. For IL calculations, Li et al. [31] suggested that the density function of the Minnesota family [32] (e.g., M06-2X) with a diffusion function basis set (e.g., 6-311++G(d,p)) might give reasonable results. If dispersion-corrected density functionals (e.g., gd3bj, DFT-D3) were used, more reliable results could be obtained [33]. Therefore, the geometry optimization and frequency analysis of all ILs and IL mixtures were performed at the M06-2X/6-311++G(d,p) level and correction with Grimme’s method. In order to calculate the interaction energy of the IL complexes, the basis set superposition error (BSSE) method was employed to correct the energy results [34]. The effect of the solvent should be taken into consideration in the theoretical calculation of the ionic liquids. It was found that the SMD solvation model proposed by Truhlar et al. can be used for the IL calculation very well [35,36]. Thus, the density functional theory (M06-2X and dispersion-corrected method) with the SMD model was also used to calculate the interaction energy of IL–CO₂/SO₂.

4. Conclusions

The CO₂ and SO₂ absorption of the flue gas in ionic liquids were investigated by the experimental method and theoretical calculation. The single ionic liquids, such as [NH₃emim][BF₄] and [C₄mim][OAc], all showed good CO₂ absorption performance for the simulated flue gas without SO₂ interference. However, SO₂ was more likely to react with the active sites of the ILs. When SO₂ was in the flue gas, the CO₂ absorption capacity of the single ionic liquid would be significantly inhibited. It was found that the interference of SO₂ on the CO₂ absorption performance might be markedly
reduced by using the ionic liquid mixtures. The CO₂ absorption capacity of the IL mixture [C4mim][OAc]/[NH2emim][BF₄] was about 0.4 mol CO₂/mol IL even at an atmosphere of 15% CO₂/2%SO₂/83% N₂, which was greater than that of single [C4mim][OAc] (0.204 mol CO₂/mol IL). There was a competitive relationship between CO₂ and SO₂ during the absorption process. The single ILs prefer to capture SO₂ rather than remove CO₂ due to the stronger interaction energy of SO₂ and the ILs. The experimental and calculated results suggested that the [OAc] anion and [NH2emim] cation are the main active sites for CO₂ and SO₂ absorption. A lower absorption enthalpy of the IL–SO₂ or IL–CO₂系统 usually means low absorption capacity. Thus, for the IL mixture [C4mim][OAc]/[NH2emim][BF₄], the quantum calculation results indicated that [NH2emim][BF₄] might be more likely to absorb SO₂ of the flue gas and CO₂ was easily removed by the [C4mim][OAc].

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**Sample Availability:** Samples of the ionic liquids are available from the authors.