Absorption of Sulfur Dioxide by Tetraglyme–Sodium Salt Ionic Liquid

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Abstract: A series of tetraglyme–sodium salt ionic liquids have been prepared and found to be promising solvents to absorb SO₂. The experiments here show that [Na–tetraglyme][SCN] ionic liquid has excellent thermal stability and a 30% increase in SO₂ absorption capacity compared to other sodium salt ionic liquids and the previously studied lithium salt ionic liquids in terms of molar absorption capacity. The interaction between SO₂ and the ionic liquid was concluded to be physical absorption by IR and NMR.

Keywords: SO₂ removal; ionic liquid; recyclable absorption; tetraglyme

1. Introduction

SO₂ (sulfur dioxide) is considered to be one of the inevitable atmospheric pollutants of industrial production. SO₂ has a number of environmental and health issues and is identified as one of the most important variables to cause hazy weather [1,2]. Thus, the control of SO₂ emission has been a serious global concern for the last century. As more countries pay extensive attention to environmental protection, limits of SO₂ emissions in flue gas are becoming more stringent. Among the desulfurization technologies, calcium-based FGD technology is a popular method [3–5]. However, the operating cost is an issue. Furthermore, a large amount of gypsum formed in the FGD process has low quality, often clogs the pipeline, and is a secondary pollutant since its permeation is harmful to the soil and groundwater. Therefore, research on the removal of SO₂ by effective solvents via absorbing-stripping processes has always been a topic of interest. In particular, the development of efficient, low cost, and low volatility solvents is the key to the success of this process.

Organic solvents have recently been used for the removal of SO₂ [6,7]. However, different organic solvents have their own shortcomings. For example, although organic amines have excellent absorption performance, they are difficult to regenerate. Regarding glycols, almost complete regeneration can be carried out at low temperature, but the absorption capacity is lower than other organic solvents. Glymes were found to have better SO₂ absorption performance than glycols due to the physical interaction between S atoms and O atoms [8,9]. However, high volatility is one of the major disadvantages of glymes.

Ionic liquids, as a new type of solvent have been further developed for their irreplaceable advantages, such as low saturated vapor pressure and high thermal and chemical stability [10]. Ionic liquids have been used in catalytic processes [11], material synthesis [12], gas detection [13], and separation of mixtures, such as CO₂ [14], H₂S [15], NO₂ [16], and CH₄ [17] absorption. Different ionic liquids, including guanidinium [18–20], imidazolium [21–23], hydroxyl ammonium [24,25], pyridinium [26], tetrabutyl ammonium [27], and phosphonium [28] have been used in SO₂ absorption. These ionic liquids have disadvantages, such as high cost, complexity in preparation, difficulty in regeneration, and so on. In addition, various ether-functionalized [29–31] and anion-functionalized [32–34] ionic liquids were
synthesized to improve the SO$_2$ absorption capacity and selectivity. However, most of those ionic liquids are prepared by complicated processes with high cost. This can be a significant obstacle when the ionic liquids’ effective industrial practice is seriously considered. An easily-prepared ionic liquid would have obvious advantages in the industrialization of SO$_2$ absorbents.

A series of glyme–lithium salt ionic liquids have been prepared and studied, and the simple synthetic method explored another path for the development of similar ionic liquids [35]. The interaction between Na$^+$ and organic solvents, such as crown ether [36], ethylene glycol [37], and acetamide [38], has been extensively studied recently. It was found that sodium salt ionic liquids can be formed by sodium salt dissolution in glymes [39,40].

In this paper, a series of sodium salt ionic liquids were synthesized and the performance of the ionic liquids were studied. It is noticeable that [Na–tetraglyme][SCN] ionic liquid has about 30% better absorption capacity than tetraglyme (G4), other tetraglyme-sodium salt ionic liquids, and the glyme–lithium salt ionic liquids. Moreover, the mechanism of the interaction between SO$_2$ and the ionic liquids was investigated by IR and NMR.

2. Experimental Section

2.1. Preparation of Ionic Liquids

The preparation of the ionic liquid was as follows: first, different sodium salts and tetraglyme were mixed at the stoichiometric ratio of 1:1 and then heated to a temperature of 303 K for 6 h while maintaining sufficient agitation. The solution was then dried in a vacuum drying chamber for 48 h. The resulting solution was transparent yellowish or colorless. The cation of the ionic liquid formed at this time is a supramolecular system consisting of sodium ions and neutral tetraglyme molecules. The anions of the ionic liquids are still the anions initially introduced by the sodium salts. The difference between these ionic liquids is mainly manifested in anions, and the cations have the same structure.

2.2. Absorption and Desorption of SO$_2$

The absorption experiment was carried out under 1 bar with a SO$_2$ partial pressure of 1 bar and a flow rate of 100 mL/min. During the regeneration experiment, regeneration was carried out for 30 min at 80 $^\circ$C by nitrogen stripping, and the flow rate was 100 mL/min.

3. Results and Discussion

3.1. Properties of Ionic Liquids

MS, $^1$H-NMR, $^{13}$C-NMR, and IR were used to identify the structures of the tetraglyme–Na$^+$ salt ionic liquids. Low resolution MS data for an ionic liquid consisting of NaSCN and tetraglyme is shown in Figure S1 in Supporting Information. It can be clearly seen that the [Na–tetraglyme][SCN] ionic liquid has a cationic molecular weight of about 245.1, which is the sum of the molecular weight of tetraglyme (222.28) and the molecular weight of sodium ion (22.99). This means that sodium ion and tetraglyme molecular form the supramolecular structure as the cation of these ionic liquids (shown in Figure 1).

The $^1$H-NMR data of tetraglyme and [Na–tetraglyme][SCN] ionic liquid are shown in Figure 2. After the form of the ionic liquid, the chemical shift has undergone a significant change, which is mainly due to the interaction of the sodium ion with the oxygen atoms in the tetraglyme molecular to reduce the deshielding effect of the oxygen atom. In contrast, the chemical shifts of the carbon atoms are basically unchanged after the form of the ionic liquid (seen in the $^{13}$C-NMR data in Figure 3). This means that the carbon atoms may not be involved in the interaction with the sodium ions in the formation of the supramolecular structure. The NMR data further confirmed the cationic structure of the ionic liquid (shown in Figure 1).
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Figure 1. Structure of [Na–tetraglyme]+ ion before and after SO2 absorption.

Figure 2. 1H-NMR spectra of tetraglyme, tetraglyme after SO2 absorption, [Na–tetraglyme][SCN] and [Na–tetraglyme][SCN] after SO2 absorption, with CDCl3 as an external reference.

Figure 3. 13C-NMR spectra of tetraglyme, tetraglyme after SO2 absorption, [Na–tetraglyme][SCN] and [Na–tetraglyme][SCN] after SO2 absorption, with CDCl3 as an external reference.
It can be seen from the IR spectra in Figure 4 that when tetraglyme forms ionic liquid with NaSCN, there is no significant shift in the C–O vibration peak at 1110 cm⁻¹ and the C–C vibration peak at 1430 cm⁻¹. A closer comparison of the spectra of the two materials reveals another difference: the ionic liquid has a distinct absorption peak at 2064 cm⁻¹, which is the absorption peak of SCN⁻.

An important purpose of tetraglyme for forming ionic liquids is to increase the thermal stability of the absorbing solvents. As seen from Figure 5, the thermal stability of [Na–tetraglyme][SCN] ionic liquid is significantly improved compared to tetraglyme. The Tₐ increases from 371 K of tetraglyme to 433 K of [Na–tetraglyme][SCN] ionic liquid. In addition, the mass of [Na–tetraglyme][SCN] ionic liquid remains stable at 373 K, while the tetraglyme is linearly reduced (seen from Figure S2). This means that [Na–tetraglyme][SCN] ionic liquid can be applied to SO₂ absorbing and regeneration without an obvious solvent loss when operating in the absorption and regeneration temperature range (i.e., 293 K to 353 K), which undoubtedly opens up the possibility of industrial application of those ionic liquids.
3.2. Absorption Capacity of Ionic Liquids

Figure 6 shows a comparison of the absorption of SO$_2$ by tetraglyme and [Na–tetraglyme][SCN] ionic liquid at different temperatures at one atmosphere. A comparison of the absorption at each temperature indicates a significant increase in the amount of SO$_2$ absorbed by the ionic liquid compared to tetraglyme alone. For example, one mol [Na–tetraglyme][SCN] ionic liquid can absorb 2.72 mol SO$_2$ at 293 K, while tetraglyme can absorb 2.10 mol SO$_2$ under the same conditions. This means the absorption capacity of the ionic liquid is improved by about 30% over tetraglyme. Moreover, the absorption capacity of both tetraglyme and the ionic liquid decreases as the temperature increases, because SO$_2$ tends to exist in the form of gas in high temperature.

Figure 6. SO$_2$ absorption capacities of tetraglyme and [Na–tetraglyme][SCN] at different temperatures with the pressure of SO$_2$ equal to 1 bar.

The absorption capacity of tetraglyme and [Na–tetraglyme][SCN] ionic liquid under different partial pressures of SO$_2$ was also investigated and the results are shown in Figure 7. As the partial pressure of SO$_2$ increases, the absorption capacity for SO$_2$ of both tetraglyme and [Na–tetraglyme][SCN] ionic liquid increases, and this increase is linear. At the same time, the absorption capacity of [Na–tetraglyme][SCN] ionic liquid is always higher than that of tetraglyme alone at the same temperature and partial pressures.

Figure 8 shows a comparison of the SO$_2$ absorption capacity of ionic liquids formed by tetraglyme with several different anionic salts. The saturated SO$_2$ absorption of tetraglyme, [Na–tetraglyme][BF$_4$] and [Na–tetraglyme][ClO$_4$] ionic liquid is 2.10, 2.11, and 2.13 mol per mol solvent, respectively, at the temperature of 293 K and 1 bar. Correspondingly, [Li–tetraglyme][NTf$_2$] has a similar SO$_2$ absorption capacity to the above ionic liquids of 2.12 mol per mol solvent [35]. As a comparison, the saturated absorption of [Na–tetraglyme][SCN] ionic liquid is 2.72 mol per mol solvent, which is about 30% higher than that of other anionic ionic liquids under the same conditions. It suggests that the type of anion has an important influence on the SO$_2$ absorption capacity of the ionic liquid, which is different from previous research [35]. The anion SCN$^-$ plays an important role in the absorption of SO$_2$.

In addition, the effects of oxygen and water on the absorption of ionic liquids have also been studied. The results show that oxygen has little effect on the SO$_2$ absorption capacity of [Na–tetraglyme][SCN] ionic liquid, as shown in Figure S3. The effect of ionic liquids with different water contents on the absorption capacity of SO$_2$ is shown in the Figure S4. As the water content in the ionic liquid increases, the absorption capacity of the ionic liquid increases slightly, rather than decreases. This shows that the participation of water does not hinder the ability of ionic liquids to absorb SO$_2$. In summary, the above experiments show that such ionic liquids have good oxygen and water resistance, which is also a required characteristic that can be considered for future industrial desulfurization absorbents.
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As the pressure of SO₂ increases, the absorption capacity for SO₂ of both tetraglyme and [Na–tetraglyme][SCN] ionic liquid increases, and this increase is linear. At the same time, the absorption capacity of [Na–tetraglyme][SCN] ionic liquid is always higher than that of tetraglyme alone at the same temperature and partial pressures.

**Figure 7.** SO₂ absorption capacities of tetraglyme and [Na–tetraglyme][SCN] at different SO₂ partial pressures.

**Figure 8.** SO₂ absorption capacities of tetraglyme, [Li–tetraglyme][NTf₂] ionic liquid, and [Na–tetraglyme][X] ionic liquids at 293 K and 1 bar (X = BF₄, ClO₄, and SCN).

3.3. Regeneration

Tetraglyme and [Na–tetraglyme][SCN] ionic liquid were also used in absorption and regeneration tests, as shown in Figure 9. The result shows that regardless of tetraglyme and the ionic liquid, the solvents maintain good absorption and regeneration performance, and the SO₂ absorption capacity of the ionic liquid is always higher than that of tetraglyme by about 30%. In all the five cycles, both tetraglyme and the ionic liquid have a low sulfur dioxide content after the regeneration. The difference of SO₂ content in the solvents in the absorbing/regenerating cycles can lead to the conclusion that [Na–tetraglyme][SCN] ionic liquid is more effective for future applications than tetraglyme.
were characterized, and their absorption capacities of SO\textsubscript{2} were tested. In addition, the interaction between SO\textsubscript{2} and the ionic liquids were investigated. The formed [Na–tetraglyme]\[SCN\] can not only significantly improve the thermal stability of the solvent but also effectively reduce solvent volatilization. It is clear that the ionic liquids mentioned above, especially [Na–tetraglyme]\[SCN\] ionic liquid, are excellent SO\textsubscript{2} absorbents, considering both the good absorption and impressive regeneration performance. Moreover, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, and IR were applied to further investigate the interaction between these ionic liquids and SO\textsubscript{2}. The IR spectral result shows that no new peak appeared after the absorption of SO\textsubscript{2} (seen in Figure 4), i.e., no new chemical bond is formed. This means that there is no chemical interaction between SO\textsubscript{2} and the sodium salt ionic liquid, which is consistent with the previous experimental results and is consistent with the conclusions from the literature on the absorption of tetraglyme [9]. That is to say, the formation of ionic liquids does not fundamentally change the nature of absorption. The \textsuperscript{1}H-NMR result in Figure 2 shows that the chemical shift changes of tetraglyme and [Na–tetraglyme]\[SCN\] ionic liquid are similar after absorption of SO\textsubscript{2}, which means that tetraglyme and [Na–tetraglyme]\[SCN\] ionic liquid have the similar mechanism of interaction between the solvents and SO\textsubscript{2}, based on the charge-transfer interaction between sulfur atoms in SO\textsubscript{2} and oxygen atoms in tetraglyme. The \textsuperscript{13}C-NMR result in Figure 3 further confirms this mechanism. Only the chemical shift moves upfield after the absorption of SO\textsubscript{2}, which suggests that there is Van der Waals’ force between SO\textsubscript{2} and SCN\textsuperscript{−}. In other words, SCN\textsuperscript{−} plays a significant role in the SO\textsubscript{2} absorption process of the [Na–tetraglyme]\[SCN\] ionic liquid.

4. Conclusions

In conclusion, a series of tetraglyme–sodium salt ionic liquids were prepared. Their structures were characterized, and their absorption capacities of SO\textsubscript{2} were tested. In addition, the interaction between SO\textsubscript{2} and the ionic liquids were investigated. The formed [Na–tetraglyme]\textsuperscript{+} can not only significantly improve the thermal stability of the solvent but also effectively reduce solvent volatilization. It is clear that the ionic liquids mentioned above, especially [Na–tetraglyme]\[SCN\] ionic liquid, are excellent SO\textsubscript{2} absorbents, considering both the good absorption and impressive regeneration performance. Moreover, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, and IR were applied to analyze the absorption mechanism of SO\textsubscript{2} absorption in these ionic liquids. The results suggest that charge-transfer interaction between sulfur atoms and oxygen atoms is the main force, and the Van der Waals’ force between SCN\textsuperscript{−} and SO\textsubscript{2} also plays an important role. As a conclusion, tetraglyme–sodium salt ionic liquids with high thermal stability and excellent SO\textsubscript{2} absorption capacity can be picked out as promising alternatives to the traditional SO\textsubscript{2}-absorbing agents in SO\textsubscript{2} removal.
Supplementary Materials: The following are available online. Figure S1: Mass spectrogram of [Na-tetraglyme][SCN] ionic liquid. Figure S2. Thermal gravimetric analysis of tetraglyme and [Na-tetraglyme][SCN]. (At the constant temperature of 373 K). Figure S3. SO$_2$ absorption capacities of tetraglyme and [Na-tetraglyme][SCN] at different SO$_2$ partial pressures. (SO$_2$ was diluted by N$_2$ or air). Figure S4. SO$_2$ absorption capacities of [Na-tetraglyme][SCN] with different water contents at 293 K and 1 bar.

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**Sample Availability:** Samples of the compounds including tetraglyme, NaSCN and NaBF4 are available from the authors.