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CO₂ capture by alcohol ammonia based deep eutectic solvents with different water content

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Abstract

The existing CO₂ absorption by deep eutectic solvents is limited by the unavoidable water absorption problem during use. In this study, we prepared three deep eutectic solvents with different alcohol aminations and added different water contents to discuss the effect of water content on the absorption of carbon dioxide by deep eutectic solvents. All deep eutectic solvents have a low melting point at room temperature as a liquid and have high thermal stability, where the choline chloride-diethanolamine deep eutectic solvents have a high viscosity. Anhydrous choline chloride-monoethanolamine deep eutectic solvents have the largest CO₂ absorption, reaching 0.2715 g g⁻¹, and the absorption of CO₂ by anhydrous choline chloride-N-methyl diethanolamine deep eutectic solvents is only 0.0611 g g⁻¹. Water content inhibited the absorption of CO₂ in primary amine and secondary amine systems, whereas it enhanced the absorption of CO₂ in tertiary amine systems, which was related to the reaction process of deep eutectic solvent and CO₂.

1. Introduction

Emissions of greenhouse gases have caused many environmental problems, where CO₂ has a considerably effect. Capturing CO₂ from the environment has become a key issue in preventing global warming and climate change; most of the effort in capturing CO₂ capture are focused on fossil fuel-based postcombustion capture [1]. As the most common method of CO₂ capture, solvent absorption has the advantages of rapid reaction and simple synthesis. Martins demonstrated that cholinium lysinate ionic liquid has high CO₂ capture capability [2]. Alcohol ammonia solution (such as monoethanolamine, MEA) is still the most common absorber of CO₂ [3] despite the emergence of many new absorbers. However, alcohol ammonia solution decomposes at high temperature, produces volatile substances [4], corrodes equipment, and causes other problems during use, thereby increasing the use cost of alcohol ammonia solution. This condition has prompted the search for an alternative to the traditional alcohol ammonia solution.

Deep eutectic solvents (DES) [5, 6] are a new liquid system formed by hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA), and their melting point is significantly lower than any component. DES is considered a substitute for traditional ionic liquids due to its green, cheap, and easy preparation characteristics [7, 8]. The component of DES is controllable and can be designed as the absorbent of specific gases, such as CO₂ [9], SO₂ [10–12], and H₂S [13, 14]; thus, it can be used in gas separation [15–18]. Adeyemi [19] prepared a series of different amino groups of DES, where choline chloride-monoethanolamine (ChCl-MEA) has the highest absorption capacity for CO₂. Ahmad [20] developed three N-methyl diethanolamine (MDEA)-based DESs with high CO₂ absorption capacity. Zhang [21] studied imidazole-derived task-specific DES based on a protic ionic liquid, and its CO₂ adsorption capacity reached 1.00 mol CO₂/mol DES. Many studies have shown that DES has high efficiency in CO₂ adsorption, especially alcohol ammonia-based DES [22, 23].

The water content of DES has a significant effect on its related physicochemical properties, and most DESs draw water from the air [24, 25], and the existence of water affects the capture effect of CO₂. Therefore, studying the influence of water content on the CO₂ adsorption of DES for practical application is of great importance.

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However, few reports are available in this regard at present. Studies have shown that a small amount of water increases the absorption of CO$_2$, but the continued increase in water content reduces the absorption of CO$_2$ [26]. In Li’s study [27], 10 wt% water content increased the CO$_2$ solubility of a range of ethanolamine-based DES. These results indicate that the influence of water content on the absorption of CO$_2$ by DES is closely related to the composition of DES.

In this work, we prepared the DES of ChCl and different alkyl amine solutions for capturing CO$_2$. Different from previous studies, we systematically characterized the prepared DES and studied its related physical and chemical properties. We investigated the influence of different water contents on the adsorption of CO$_2$.

2. Experimental section

2.1. Materials
ChCl (AR $\geq$ 98%), diethanolamine (DEA, AR $\geq$ 99%), and MDEA (AR $\geq$ 98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. MEA (AR $\geq$ 99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. All materials were used for the preparation of DES without further purification. CO$_2$ (99.999%) was obtained from Guizhou Sanhe Gas Co., Ltd.

2.2. Preparation of DES
The DES synthesis method was the same as previously reported [28, 29]. With ChCl as HBA and different alcohol ammonia solution as HBD, a certain molar ratio (ChCl: MEA $=$ 1:5; ChCl: DEA $=$ 1:6; ChCl: MDEA $=$ 1:7) was mixed at 60°C for several hours to form DES.

2.3. Characterization
The melting points of DES was measured through differential scanning calorimetry (TAQ2000) under the protection of N$_2$. The viscosity was measured with a falling ball-type viscometer (Lovis 2000 M). The thermal stability of ionic liquids was measured with a thermogravimetric analyzer (TGA5500). The structure of DES was studied through Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50) and nuclear magnetic resonance (NMR, Joel ECX500) analysis.

2.4. CO$_2$ absorption
The CO$_2$ capture experiment was completed by using a gas absorption platform. The experimental device is shown in figure 1. The CO$_2$ absorption capacity of DES was obtained by weighing method. The total weight of the absorption bottle and DES (mass: 2 g) was $M_0$, and the total weight of the absorption bottle and DES was measured every 10 min, denoted as $M_n$, and repeated for 6 times. $M$ denotes the CO$_2$ absorption, and its formula is as follows:

$$M = \frac{(M_n - M_0)}{2}$$
3. Results and discussion

3.1. Melting point
Melting point is an important property of DES. The HBD and HBA form DES through hydrogen bond action, making the melting point of DES lower than the melting point of any of its components [30, 31]. The melting point of the DES in this work is shown in figure 2(b). The crystallization and melting peaks of DES can be clearly observed from figure 2(b). The melting point of ChCl-MEA is 4.54 °C, the melting point of ChCl-DEA is 20.82 °C, and the melting point of ChCl-MDEA is −27.35 °C, which are all lower than the melting point of its single component.

3.2. Viscosity
Viscosity has a great influence on the practical application of absorbents. The increase in viscosity leads to the decrease in heat transfer of gas mass and reduces the absorption effect of absorbent. The viscosity of the DES is shown in figure 2(c). The viscosities of ChCl-MEA and ChCl-MDEA are lower than that of ChCl-DEA, and ChCl-MEA has the least viscosity. The increase in temperature can reduce the viscosity of the DES. The viscosity of ChCl-DEA is most affected by the temperature change. The viscosity is 341.01 mPa·s at 30 °C and 25.025 mPa·s at 80 °C.

3.3. Thermal stability
The thermal stability of DES is different from that of ionic liquids. In the process of heating, the hydrogen bond in the DES breaks first, and then the HBD with poor thermal stability loses weight [24]. When the temperature continues to rise, HBA decomposition phenomenon occurs, and then the DES loses weight in the heating process. In figure 2, the thermal decomposition process of DES presents the phenomenon of distributed decomposition. The total decomposition temperature of MEA is the lowest and that of DEA is the highest. DES is decomposed in two steps during heating. The first step decomposition of ChCl-MEA, ChCl-DEA, and
ChCl-MDEA is at 137 °C, 200 °C, and 182 °C, respectively, and the second step decomposition is at 295 °C, 287 °C, and 293 °C, respectively. The results show that DES has better thermal stability.

3.4. FT-IR spectra of DES

Normalized FT-IR spectra for the ChCl-MEA DES along with those for their two pure constituents are shown in figure 3(b). Pure ChCl shows several functional groups, the vibrational bands at 1092 and 1134 cm\(^{-1}\) refer to the C–O and C–N symmetric stretching, and the vibrational band at 948 cm\(^{-1}\) refer to the C–C asymmetric stretching [32]. For pure MEA, vibrational bands at 1033 and 1471 cm\(^{-1}\) refer to the C–O and C–H stretching. The vibrational band at 1597 cm\(^{-1}\) represents the bending vibrations of N–H in primary amine. The vibrational band widens at 3200–3400 cm\(^{-1}\), indicating hydrogen bond formation after the DES formation [33]. For pure DEA (figure 3(c)), vibrational bands at 940, 1456 and 1652 cm\(^{-1}\) refer to C–C, C–H and C–N stretching. For pure MDEA (figure 3(d)), vibrational bands at 1034, 1083 and 1456 cm\(^{-1}\) refer to C–OH, C–N and C–H stretching [34].

After the absorption of CO\(_2\), the structure of ChCl–MEA and ChCl–DEA changed. The infrared spectrum showed that a new characteristic peak of ChCl-MEA appeared at 1541 cm\(^{-1}\), indicating the emergence of new functional groups, and the characteristic peak of N–H stretching in the primary amine at 3389 cm\(^{-1}\) was weakened [35]. Carbamate was formed after the absorption of CO\(_2\). Similar to ChCl-MEA, the characteristic peak strength of ChCl-DEA at 3300–3400 cm\(^{-1}\) was weakened, and the characteristic peak of carbamate appeared at 1541 cm\(^{-1}\). Chemical absorption occurs in the absorption of CO\(_2\) by ChCl-MEA and ChCl-DEA, and carbamate is formed.

The infrared spectrum results of ChCl-MDEA did not show new functional groups after the absorption of CO\(_2\), and no chemical reaction occurred between CO\(_2\) and ChCl-MDEA, indicating that CO\(_2\) absorption by ChCl-MDEA was only physical absorption. This condition is completely different from the absorption of CO\(_2\) by ChCl-MEA and ChCl-DEA.
3.5. NMR analysis of DES

The $^{13}$C NMR results showed that the peaks that appeared at 57.32 and 67.29 ppm corresponded to $\text{--CH}_2\text{OH}$ and $\text{--NH}_2\text{CH}_2$, and the peaks at 53.48 ppm were attributed to $\text{--CH}_3$ in ChCl [36]. For MEA, the peaks at 44.64 and 63.76 ppm were attributed to $\text{--NCH}_2$ and $\text{--CH}_2\text{OH}$, respectively (figure 4(a)). For DEA, the peaks at 52.11 and 60.73 ppm were attributed to $\text{--NHCH}_2$ and $\text{--CH}_2\text{OH}$, respectively (figure 4(c)) [37]. For MDEA, the peaks at 41.72, 59.16 and 62.37 ppm were attributed to $\text{--CH}_3$, $\text{--NH}_2\text{CH}_2$ and $\text{--NCH}_2$, respectively (figure 4(e)) [20, 38]. The $^1$H NMR results showed that the peaks at 3.16, 3.44 and 3.81 ppm corresponded to $\text{--CH}_3$, $\text{--NH}_2\text{CH}_2$ and $\text{--CH}_2\text{OH}$ in ChCl [36]. The peaks at 2.29 and 3.09 ppm corresponded to $\text{--NHCH}_2$ and $\text{--CH}_2\text{OH}$ in MEA (figure 4(b)). For DEA, the peaks at 2.61 and 3.48 ppm were attributed to $\text{--NHCH}_2$ and $\text{--CH}_2\text{OH}$, respectively (figure 4(d)) [37]. For MDEA, the peaks at 2.14, 2.37, 3.41 and 4.31 ppm were attributed to $\text{--CH}_3$, $\text{--NCH}_2$, $\text{--CH}_2$ and $\text{--OH}$ respectively (figure 4(f)) [20]. Compared with before and after the formation of DES, no new peak appeared, indicating that the formation of DES is a physical process.

After the absorption of CO$_2$, the characteristic peak of carbamate appeared in ChCl-MEA and ChCl-DEA at 162.09 ppm of $^{13}$C NMR in figures 4(b)–(d), indicating that carbamate was generated after the absorption of
CO2. Similarly, the characteristic peak of carbamate appeared at 5.86 ppm of 1H NMR in figures 4(b)–(d) [35, 38]. Compared with ChCl-MEA and ChCl-DEA, no new peaks were observed after the absorption of CO2 in ChCl-MDEA, indicating no carbamate was formed.

3.6. CO2 capture
In figure 5, ChCl-MEA has the largest adsorption capacity for CO2 due to the chemisorption of CO2, and the absorption amount of CO2 is 0.2715 g g\(^{-1}\) after 60 min of reaction, followed by ChCl-DEA, which is 0.1713 g g\(^{-1}\). The results higher than the [HDBU][Im]/EG DES (0.141 g g\(^{-1}\)) and most of the reported IL-based DESs absorption of previous work [39]. However, the absorption amount of CO2 is only 0.0611 g g\(^{-1}\) after 60 min reaction because ChCl-MDEA only has physical adsorption on CO2.

In accordance with relevant studies, MEA and DEA react with CO2 to generate carbamate in the subsequent reaction process, as shown in figure 3(a). This condition is because primary amine and secondary amine can react directly with CO2, which is divided into two steps [7].

First step:

\[ \text{CO}_2 + R_1R_2NH \rightleftharpoons R_1R_2NHC\text{OOH} \]

Second step:

\[ R_1R_2NHC\text{OOH} + R_1R_2NH \rightleftharpoons R_1R_2N\text{COO}^- + R_1R_2NH_2^+ \]

The increase in viscosity decreases the mass transfer and free matter migration, resulting in a decrease in the absorption rate of CO2. The viscosity of ChCl-DEA is greater than that of ChCl-MEA. Thus, the amount of CO2 absorbed by ChCl-DEA is less than that of ChCl-MEA, which is reasonable.

We studied the influence of water content on CO2 absorption by ChCl-MEA and ChCl-DEA. The results are shown in figures 5(b)–(c). The addition of water reduced the absorption of CO2 by ChCl-MEA and ChCl-DEA,
and the inhibition effect became more obvious with the increase in water content. The addition of water destroys the hydrogen bond network and reduces the concentration of amino groups. Therefore, the presence of water for the DES with primary amines and secondary amines greatly inhibits the absorption of CO₂.

ChCl-MDEA has only physical adsorption of CO₂. Thus, its absorption is less than that of ChCl-MEA and ChCl-DEA. This condition is because the reaction between tertiary amine and CO₂ requires the participation of water [40, 41]. The reaction process is as follows:

\[
R_1R_2R_3NH + CO_2 + H_2O \rightleftharpoons HCO_3^- + R_1R_2R_3NH_2^+
\]

No water is found in the ChCl-MDEA system. Thus, only physical adsorption of CO₂ occurs. Therefore, the influence of different water contents on the adsorption effect of CO₂ is studied, and the results are shown in figure 5(d).

When water was added to the system, the CO₂ absorption of the 10 wt% H₂O system is 0.0834 g g⁻¹ after 60 min of reaction, indicating that chemical adsorption occurred in addition to physical adsorption. When the water content continued to increase, the CO₂ absorption decreased but still greater than that of the anhydrous system with only physical adsorption, indicating that water had a promoting effect on the system’s absorption of CO₂.

4. Conclusion

In the present work, we found that water content significantly affects the absorption capacity of CO₂ by DES. DES containing primary amine and secondary amine reduces the amount of CO₂ absorption with the increase in water content. The DES containing tertiary amine produces chemical adsorption after adding water, increasing the absorption of CO₂. However, the larger water content still reduces the absorption of CO₂. The formation of carbamate in chemisorption is determined through FT-IR and NMR analyses. Studies on the physicochemical properties of DES show that ChCl-MEA with lowest viscosity has the highest CO₂ adsorption capacity, and all DESs have high thermal stability and lower melting point.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare no conflict of interest.

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