Hydrophobic Functional Deep Eutectic Solvents Used for Efficient and Reversible Capture of CO2

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ABSTRACT: CO2 emission from flue gas is an important issue threatening human survival. Deep eutectic solvents (DESs), which have many unique properties, have been studied for CO2 capture. However, water can be absorbed by DESs during the absorption of CO2, which may increase the energy cost during the desorption of CO2. In this work, a new kind of hydrophobic functional DES formed by polyamine hydrochloride and thymol was synthesized and used for CO2 capture. It had been found that these DESs could efficiently capture CO2 even at low partial pressures. The CO2 capacity of [TEPA]Cl-thymol (n_{[TEPA]Cl}/n_{thymol} = 1:3) was high up to 1.355 mol CO2/mol DES at 40 °C and 101.3 kPa. Interestingly, these DESs were still hydrophobic after saturated with CO2. The CO2 absorption capacity increased with a decrease of temperature and an increase of CO2 partial pressure. Regeneration results showed that no obvious loss in the capacity could be found after five absorption/desorption cycles of these DESs. The Fourier transform infrared (FT-IR) spectra indicated that CO2 could interact with amino in the DESs by the formation of carboxylate. Moreover, the equilibrium constant and Henry’s law constant in chemical absorption and physical absorption were studied.

INTRODUCTION

Carbon dioxide (CO2), mainly emitted from the burning of fossil fuels and energy-related processes in the industry, is one of the major greenhouse gases.1,2 CO2 in flue gas with contents up to 10−15 vol % poses a direct threat to the environment and human health. Therefore, it is important to develop recyclable absorbents to capture CO2 from flue gas with high capacity and low volatility.

In commercial processes, amine solutions are the most commonly used reversible solvents for CO2 capture.4 Considering the economic and environmental problems, such as the corrosion of equipment, the loss of amines, and high energy cost during the recovery process, new solvents with low volatility and energy cost should be developed.

Ionic liquids (ILs), which have many unique properties, such as high thermal stability, negligible vapor pressure, high CO2 capacity, and adjustable structure,6 are good candidates for CO2 absorption.7−13 Normal ILs,14−16 which only have physical interaction with CO2, can hardly be used for CO2 capture from flue gas. Functional IL for CO2 absorption was first reported by Davis et al.,6 and the CO2 capacity could reach almost 0.5 mol CO2/mol IL at 22 °C and ambient pressure. In recent decades, more and more functional ILs were synthesized, such as amine-based ILs,17,18 imidazole-based ILs,19,20 and carboxyl-based ILs.21 Functional ILs have high CO2 capacity even under low CO2 partial pressures, but some disadvantages still exist, such as high viscosity, complicated synthesis process, and high cost.

Recently, deep eutectic solvents (DESs), mainly synthesized by hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), have been widely investigated in CO2 capture.22−29 DESs have similar properties to ILs and can avoid some defects of ILs. Normal DESs could achieve high CO2 absorption by physical dissolution at high CO2 partial pressures.23,30,31 Choline chloride-based (ChCl) DESs could absorb CO2 at high CO2 partial pressures, and the solubility of CO2 in phenol-ChCl DES (n_{phenol}/n_{ChCl} = 2:1) could reach up to 0.18 mol CO2/mol DES at 40 °C and 503 kPa. However, the solubility decreased greatly to just 0.0033 mol CO2/mol DES at 122 kPa. To capture low-partial-pressure CO2 with high capacity, functional DESs were investigated. Cui et al.25 reported that functional DESs made up of [P2222][Triz] as an HBA and ethylene glycol (EG) as an HBD exhibited a high CO2 absorption capacity of 0.91 mol CO2/mol DES for [P2222][Triz]-EG DES (n_{[P2222][Triz]}/n_{EG} = 1:2) at 25 °C and ambient pressure. In our previous work, functional DESs with polyamine hydrochloride as an HBA and EG or DG as an HBD were synthesized.32 Among the DESs, [TETA]Cl-EG...
DES ($n_{[TETA]Cl}/n_{thymol} = 1:3$) had an excellent CO$_2$ capacity of 1.456 mol CO$_2$/mol DES at 40 °C and ambient pressure. As we know, moisture exists in flue gas with the contents of 8—20 vol %.$^{33$—$35$} During the capture of CO$_2$, moisture in flue gas can also be absorbed by DESs. Hydrophilic DESs can absorb a large amount of water during the capture of CO$_2$, which can greatly reduce the mass absorption capacity in the CO$_2$ desorption process. Therefore, it is necessary to synthesize and use hydrophobic DESs to capture CO$_2$ from flue gas. Nowadays, hydrophobic DESs have been used in many fields, such as liquid—liquid microextraction$^{37$—$40$} and gas—gas separation.$^{41$—$42$} Zubeir et al.$^{41}$ synthesized hydrophobic DESs using decanoic acid (DecA) as an HBD and five different quaternary ammonium salts as an HBA to absorb pure CO$_2$. As no functional group existed in the DESs, the capacity of CO$_2$ in the DESs was very low under low pressures, just 0.015 mol CO$_2$/mol DecA—[N8888]Cl DES ($n_{DecA}/n_{[N8888]Cl} = 1:5$) at 35 °C and 0.09 MPa as an example. However, due to only physical interaction between CO$_2$ and these normal hydrophobic DESs, these DESs cannot be used for CO$_2$ capture from flue gas.

To capture CO$_2$ from flue gas and decrease energy cost, a novel kind of hydrophobic functional DES, as shown in Figure 1, was synthesized and used for CO$_2$ capture in this work.

### RESULTS AND DISCUSSION

**Miscibility of DESs with Water.** The solubilities of water in [TETA]Cl-thymol DESs and [TEPA]Cl-thymol DESs before and after CO$_2$ absorption were measured and are shown in Table 1. The solubilities of water in [TETA]Cl-thymol DES ($n_{[TETA]Cl}/n_{thymol} = 1:3$) and [TEPA]Cl-thymol DES ($n_{[TEPA]Cl}/n_{thymol} = 1:3$) were 0.051 and 0.062 g/g DES, respectively. This indicated that these DESs were hydrophobic.

Interestingly, these DESs were still hydrophobic after being saturated with CO$_2$. After CO$_2$ absorption, the solubilities of water in [TETA]Cl-thymol DES ($n_{[TETA]Cl}/n_{thymol} = 1:3$) and [TEPA]Cl-thymol DES ($n_{[TEPA]Cl}/n_{thymol} = 1:3$) were 0.053 and 0.069 g/g DES, respectively. This means that absorbed CO$_2$ hardly changes the water solubility in the DESs, even if a new chemical bond between DES and CO$_2$ may be formed.

Compared with the reported work$^{32}$ [TETA]Cl—EG DES and [TETA]Cl—DG DES are two kinds of hydrophilic DESs, but [TETA]Cl—thymol DES is a kind of hydrophobic DESs. This means that thymol may play a key role on the hydrophobicity of DESs.

**Volatility and Physical Properties of DESs.** Figure 2 shows the weight losses of [TETA]Cl-thymol ($n_{[TETA]Cl}/n_{thymol} = 1:3$) and [TEPA]Cl-thymol ($n_{[TEPA]Cl}/n_{thymol} = 1:3$) as a function of time at 100 °C and a N$_2$ flow of 40 mL/min.

Table 1. Density, Viscosity, and Water Content of [TETA]Cl-thymol DESs, [TEPA]Cl-thymol DESs, [TETA]Cl, and [TEPA]Cl before and after CO$_2$ Absorption at 50 °C

| DES System | $n_{[TETA]Cl}/n_{thymol}$ | $\rho$ (g/mL) before | $\eta$ (mPa·s) before | $C_{water}$ (g/g DES) before | $\rho$ (g/mL) after | $\eta$ (mPa·s) after | $C_{water}$ (g/g DES) after |
|------------|---------------------------|----------------------|-----------------------|-----------------------------|----------------------|----------------------|-----------------------------|
| [TETA]Cl-thymol DES | 1:3 | 1.0317 | 205.1 | 0.051 | 1.0485 | 6.77 × 10$^3$ | 0.053 |
| [TETA]Cl-thymol DES | 1:3 | 1.0513 | 295.7 | 0.062 | 1.0588 | 1.68 × 10$^4$ | 0.069 |
| [TETA]Cl-thymol DES | 1:5 | 1.0230 | 69.1 | 0.071 | 1.0339 | 587.4 | 0.065 |
| [TEPA]Cl-thymol DES | 1:3 | 1.0421 | 198.8 | 0.067 | 1.0533 | 1.74 × 10$^3$ | 0.059 |
| [TETA]Cl | 1:3 | 1.1329 | 1.18 × 10$^3$ | | | | |
| [TEPA]Cl | 1:3 | 1.1631 | 1.10 × 10$^4$ | | | | |
showed lower volatility than [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3))\). The low volatility of these DESs may be attributed to the hydrogen bonding between an HBA and an HBD and is an excellent property for the application of these DESs.

The density and viscosity of these DESs were also investigated. It can be seen from Table 1 that the density and viscosity of [TETA]Cl and [TEPA]Cl were very high. But when the DESs were formed with the addition of thymol, both the density and viscosity of the DESs decreased. For example, the viscosity of [TETA]Cl was \(1.18 \times 10^{-3}\) mPa·s, but the viscosity of [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:5)\) was just 69.1 mPa·s. The viscosity of [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:5)\) was about 16 times lower than pure [TETA]Cl.

**Effect of HBA/HBD on CO2 Absorption in DESs.** The decrease of viscosity also enhanced the mass transfer of CO2 in an absorbent and then decreased the equilibrium time of the absorption. The effect of \(n_{HBA}/n_{HBD}\) on CO2 absorption in DESs is shown in Figure 3. Compared with pure [TETA]Cl or [TEPA]Cl, the addition of thymol could greatly shorten the absorption time to reach equilibrium. For example, when the capacity of pure [TETA]Cl was only 0.584 mol/mol absorbent at 50 °C and ambient pressure in 14 h. After the absorption, the absorbent was almost in a solid state, and the viscosity could not be measured. However, when thymol was added in [TETA]Cl to form [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3)\), the capacity of CO2 in DES could reach up to 1.282 mol CO2/mol absorbent in 4 h. The viscosity after the absorption was just 6.77 \(\times 10^{-3}\) mPa·s. Obviously, thymol could decrease the viscosity of [TETA]Cl via forming a DES, which enhanced the mass transfer of CO2 in absorbent and shortened the time to reach equilibrium.

However, the addition of thymol in DESs played a negative role on the absorption capacity of CO2. It could be seen that thymol could not enhance the capacity of CO2 in DESs as EG.\(^{32}\) Conversely, the increase of thymol in DES could decrease the capacity of CO2. For example, the mole capacity of CO2 decreased from 1.339 mol CO2/mol absorbent in [TEPA]Cl-thymol DESs \((n_{[TEPA]Cl}/n_{thymol} = 1:3)\) to 1.183 mol CO2/mol absorbent in [TEPA]Cl-thymol DESs \((n_{[TEPA]Cl}/n_{thymol} = 1:5)\).

As reported in previous work, the addition of acid in ionic liquids or solvents could decrease the capacity of acidic gases in ionic liquids or solvents.\(^{43,44}\) As we know, thymol is a weakly acidic substance, which has a phenolic hydroxyl group. This may be the reason why the addition of thymol could decrease the capacity of CO2 in DESs.

**Effect of Temperature and Partial Pressure on CO2 Absorption in DESs.** Temperature is an important issue for gas capture. Figure 4 shows the effect of temperature on the absorption of CO2 in [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3))\) and [TEPA]Cl-thymol DES \((n_{[TEPA]Cl}/n_{thymol} = 1:3)\) at ambient pressure. It could be found that both the CO2 capacity and the equilibration time decreased with increasing temperature. For example, CO2 absorption capacity decreased from 1.298 to 1.135 mol CO2/mol DES in [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3)\), when the temperature increased from 40 to 60 °C. Meanwhile, the equilibration time decreased from 9 to 4 h.

As the content of CO2 in flue gas is very low, it is necessary to study the capacity of CO2 under different partial pressures by DESs. CO2 capacities in [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3)\) and [TEPA]Cl-thymol DES \((n_{[TEPA]Cl}/n_{thymol} = 1:3)\) as the function of time with different CO2 partial pressures are shown in Figure 5. The CO2 capacity in DESs decreased with decreasing CO2 partial pressure. However, even when the CO2 partial pressure decreased to 10.1 kPa, these DESs still had very high CO2 capacity. Taking [TETA]Cl-thymol DES \((n_{[TETA]Cl}/n_{thymol} = 1:3)\), for example, the CO2 absorption capacity decreased from 1.282 mol CO2/mol DES at 101.3 kPa to 1.047 mol CO2/mol DES at 50.6 kPa, as shown in Table 2.
and 101.3 kPa. CO2 could be released from [TETA]Cl-thymol DES (n_{[TETA]Cl}\_thymol = 1:3) at 50 °C

| P (kPa)  | n | n_{hem} | n_{phys} |
|---------|---|---------|---------|
| 101.3   | 1.282 | 1.096 | 0.186 |
| 50.6    | 1.047 | 0.964 | 0.083 |
| 10.1    | 0.592 | 0.575 | 0.017 |

“P” stands for the partial pressure of CO2. “n” stands for the moles of CO2 per mole DES. “n_{hem}” stands for the moles of CO2 per mole DES with chemical absorption. “n_{phys}” stands for the moles of CO2 per mole DES with physical absorption.

Performance in [TEPA]Cl-thymol DES was similar to that in [TETA]Cl-thymol DES. These above results suggested that these DESs could be regenerated by increasing the temperature and/or decreasing the CO2 partial pressure.

Reuse of DESs. The reuse of these DESs played a key role in the application of these DESs in industry, and the results of the reuse of these DESs are shown in Figures 6 and 7. All these DESs could be reused for five cycles during the absorption of CO2 at 40 °C under N2 as sweeping gas.

Compared with other hydrophobic ILs and DESs. The summarization of hydrophobic ILs and DESs is shown in Table 3. As can be seen, the capacities of CO2 in [TETA]Cl-thymol and [TEPA]Cl-thymol DESs are much higher than those ILs and DESs reported in the references.

| absorbent | T (°C) | P_{CO2} (kPa) | CO2/mol abs | g CO2/g abs | refs |
|-----------|-------|---------------|-------------|-------------|------|
| [BMIM][PF6] | 25 | 100 | 0.019 | 0.003 | 15 |
| [TMPDA][Tf2N] | 25 | 100 | 0.026 | 0.0028 | 49 |
| [BDMAAE][Tf2N] | 25 | 100 | 0.015 | 0.0015 | 49 |
| [TMHDA][Tf2N] | 25 | 100 | 0.023 | 0.0022 | 49 |
| DecA[N$_{HBA}$]Cl$^+$ | 25 | 90 | 0.013 | 0.0024 | 41 |
| DecA[N$_{HBA}$]Br$^+$ | 25 | 90 | 0.014 | 0.0024 | 41 |
| DecA[N$_{HBA}$]Cl$^+$ | 25 | 90 | 0.013 | 0.0027 | 41 |
| DecA[N$_{HBA}$]Br$^+$ | 25 | 90 | 0.016 | 0.0024 | 41 |
| [TETA]Cl-thymol | 40 | 101.3 | 1.298 | 0.09 | this work |
| [TEPA]Cl-thymol | 40 | 101.3 | 1.355 | 0.088 | this work |

Absorption Mechanism. As mentioned above, these DESs can capture a large amount of CO2 even under low CO2 partial pressures. The molar ratio of CO2 in [TETA]Cl-thymol DES can reach up to 1.282 at 50 °C and 101.3 kPa, close to the ideal stoichiometric ratio of CO2 chemical absorption in [TETA]Cl, 1:5:1. It is noted that the ideal chemical capacity of CO2 in [TETA]Cl is 0.5 mol CO2/mol free amino. The high capacity of CO2 in DESs demonstrates that not only physical interaction but also chemical interaction exists between DESs and CO2. The increase of viscosity after the absorption of CO2 also hints that new chemical bonds appear during the absorption, and the chemical interaction is much stronger than physical interaction.

The FT-IR results in Figure 8 show the change of [TETA]Cl-thymol DES before and after CO2 absorption. Comparing the FT-IR spectra before and after CO2 absorption, a new peak appears at 1641 cm$^{-1}$ after CO2 absorption, which can be attributed to the formation of N···C==O. This means that chemical interaction exists between the amino group and CO2. In addition, there are strong peaks at 1330 and 1584 cm$^{-1}$, which are associated with the formation of carbonate $-COO^\cdot$ in DES. This means that CO2 captured by DES formed carboxylate with DES.

Based on the results above, the free amino group in [TETA]Cl may be the main reason for CO2 absorption by the DES. As no chemical bonds can be found between thymol and CO2, thymol may only physically absorb CO2 during the absorption. The absorption mechanism in this work may be similar to the previous one. A possible mechanism of CO2 absorption by these DESs is proposed and shown in Scheme 1.
For the chemical absorption, one mole free amino in DESs can chemically capture 0.5 mole CO2.

Scheme 1. Proposed Mechanism for the Reaction of CO2 and Amino in DESs

As both physical and chemical interactions exist during the absorption of CO2 in DESs, the absorption of CO2 in these DESs is the sum of the chemical and physical contributions. Therefore, the total capacity in DESs can be divided into chemical capacity and physical capacity, as shown in eq 1. There are equilibrium constant and Henry’s law constant in chemical absorption and physical absorption, respectively, at a certain temperature.

\[ n = n_{\text{phys}} + n_{\text{chem}} \]  

(1)

where \( n \) is the total mole ratio of CO2, \( n_{\text{phys}} \) is the physical capacity of CO2, and \( n_{\text{chem}} \) is the chemical capacity of CO2.

For physical absorption, the capacity of CO2 in DES obeys Henry’s law, as shown in eq 2.

\[ P = Hx_B = H \frac{n_{\text{phys}}}{1 + n_{\text{phys}}} \]  

(2)

where \( P \) is the partial pressure of CO2, \( H \) is Henry’s law constant, and \( x_B \) is the mole fraction of CO2.

As proposed above, one mole CO2 can react with two moles of free amino in DESs. To simplify Scheme 1, we represent the free amino component in DES as “A” and the CO2 component as “B”, which reduces the scheme to the following equation

\[ 2A + B \rightleftharpoons A_2B \]  

(3)

Then, the equilibrium constant, \( K^0 \), is calculated by the following equation

\[ K^0 = \frac{a_{A_2B}}{a_A f_A^{\nu} a_B f_B^{\nu}} = \frac{Y_{A_2B} C_{A_2B}}{Y_A C_A f_A^{\nu} Y_B f_B^{\nu}} = \frac{2C_A^2 f_A^{\nu}}{2C_A f_A^{\nu} / P_0} \]  

(4)

where \( a_{A_2B} \) and \( a_A \) are the activities of the A2B complex and A, respectively; \( f_B^{\nu} \) is the fugacity of B in the vapor phase; \( P_0 \) is the standard pressure; \( Y_{A_2B} \) and \( Y_A \) stand for the activity coefficients of the A2B complex and B, respectively; and \( C_{A_2B} \) and \( C_A \) are the molar concentrations of the A2B complex and A, respectively. Due to the similar property to ILs, the activity coefficients of DES are reasonably assumed to be 1 as of ILs. Then, eq 4 leads to eq 5.

\[ K^0 = \frac{C_{A_2B}}{C_A f_A^{\nu} / P_0} = \frac{C_0 - C_t}{2C_A f_A^{\nu} P_0} \]  

(5)

where \( C_0 \) is the initial molar concentration of free amino and \( C_t \) is the equilibrium molar concentration of free amino, which can be obtained by eqs 6 and 7.

\[ C_0 = \frac{3}{V} \]  

(6)

\[ C_t = \frac{3 - 2 \times n_{\text{chem}}}{V'} \]  

(7)

where \( V \) and \( V' \) are the volumes of absorbent before and after absorption, respectively. As there is no obvious volume change of absorbent before and after absorption, it is reasonable to assume that \( V \) and \( V' \) are equal. To simplify the calculation, \( f_B^{\nu} \) can be considered as equal to \( P \).

Based on eqs 1, 2, 4–6, the following equation is obtained to relate the total solubility of CO2 in DES to the partial pressure of CO2.

\[ n = \frac{P}{H - P} + \frac{12K_0^{\nu} P + V - \sqrt{24K_0^{\nu} P \cdot V + V^2}}{8K_0^{\nu} P} \]  

(8)

There are two parameters, \( H \) and \( K_0^{\nu} \), in eq 8, which should be calculated. These parameters can be obtained by fitting the experimental capacity at different CO2 partial pressures. The fitting curve for CO2 capacity in [TETA]Cl-thymol DES at 50 °C is shown in Figure 9. The experimental data show excellent agreement with the calculated data. The fitted parameters, \( H \) and \( K_0^{\nu} \), are 648 kPa and 1.073, respectively, with the correlation coefficient R2 larger than 0.9999. The physical and chemical capacities of CO2 in [TETA]Cl-thymol DES...
$\left( n_{\text{TETA(Cl)}} : n_{\text{thymol}} = 1:3 \right)$ at 50 °C are also calculated and shown in Table 2. As expected, the absorption capacity of CO$_2$ is contributed from both physical and chemical absorptions. Chemical absorption is dominate, while physical absorption is minor.

## CONCLUSIONS

In summary, a series of hydrophobic functional DESs based on polyamine hydrochloride as an HBA and thymol as an HBD were synthesized to absorb CO$_2$ from simulated flue gas. Miscibility with water and the physical properties of DESs before and after the capture of CO$_2$ were measured. Besides, the effects of the mole ratio of HBA to HBD, temperature, and CO$_2$ partial pressure on the capture of CO$_2$ in the DESs were studied. It was found that these DESs were always hydrophobic before and after the capture of CO$_2$, and the increase of thymol in DESs could decrease the viscosity and density of DESs. All these DESs could capture large amounts of CO$_2$ from simulated flue gas, and the capacity of CO$_2$ in DES could reach up to 1.355 mol CO$_2$/mol DES in [TETA]Cl-thymol DES ($n_{\text{TETA(Cl)}} : n_{\text{thymol}} = 1:3$) at 40 °C and 101.3 kPa. Decreasing temperature and increasing partial pressure could enhance the capture of CO$_2$. The results of FT-IR indicated that CO$_2$ could chemically interact with amino in DESs by the formation of carboxylate. Moreover, the equilibrium constant and Henry's law constant in chemical absorption and physical absorption were studied. It was found that both physical and chemical absorptions contributed to the total absorption capacity of CO$_2$.

## EXPERIMENTAL SECTION

### Materials.

CO$_2$ (99.999%) and N$_2$ (99.999%) were obtained from Beijing Haipu Gases (Beijing, China). Triethylenetetramine (TETA, 70% in an aqueous solution) and tetaethylpentamine (TEPA) (98%) were purchased from Aladdin (Shanghai, China). Thymol (99%) was purchased from Maclin Biochemical Co., Ltd. (Beijing, China). Hydrochloric acid (36–38%) was obtained from Beijing Chemical Plant (Beijing, China).

### Preparation of DESs.

[TETA]Cl was synthesized by a reaction between an aqueous solution of TETA and an equimolar amount of hydrochloric acid as reported in literature.$^3$ After the reaction, water was removed by a rotary evaporator at 80 °C. And then, the crude product was purged with the continuous nitrogen of 40 mL/min at 100 °C for more than 48 h, until the mass ratio of water in [TETA]Cl was less than 0.005. [TETA]Cl was mixed with thymol in an expected molar ratio at 100 °C, and then nitrogen was bubbled into the mixture for 20 min to remove the impurities in the DES. The prepared DES was then stored in a desiccator. The synthesis process of other DESs was the same as the above one.

### Volatility of DESs.

The volatility of DESs was investigated by measuring the weight loss of the DES under sweeping gas at 100 °C. In a typical experiment, about 2 g of DES was loaded in a test tube ($\phi$15 × 150 mm). Then, nitrogen gas with a flow rate of 40 mL/min was bubbled into the DES to remove volatile compounds. The weight of the test tube and the DES were measured at a regular interval by an analytical balance (BS 224S, Sartorius) with an accuracy of 0.1 mg. The DES retained in the test tube could be calculated by subtracting the weight of the test tube from the total weight of the test tube and DES.

### Properties of DESs.

The density of DESs was determined by Karl Fischer titration (ZDJ-400S, Multifunctional Titrator, Beijing Xianqu Weifeng Company, Beijing, China). The expanded uncertainty of water mass ratio was ±6.8% at the mass ratio of water = 10$^{-3}$. To learn the miscibility of DESs with water before and after the absorption, water was added into the test tube contained DESs before or after CO$_2$ absorption, until two phases appeared in the test tube. Then, the mass ratio of water in the upper phase was measured by Karl Fischer titration.

### Absorption and Desorption of CO$_2$.

The absorption and desorption of CO$_2$ were carried out at ambient pressure in a constant temperature water (or oil) bath, which was controlled within ±0.5 °C. In a typical absorption experiment, about 2 g of DES was loaded in a test tube (length 100 mm, inner diameter 15 mm). CO$_2$ gas with a flow rate of 40 mL/min at ambient pressure was bubbled into the DES in a glass tube, which was partially immersed in a constant-temperature water bath (the uncertainty was ±0.5 °C). The CO$_2$ absorption capacity was measured at regular intervals by an analytical balance with a precision of 0.1 mg. For the absorption, if CO$_2$ partial pressure was less than 101.3 kPa, pure CO$_2$ was diluted by N$_2$ to reduce the partial pressure of CO$_2$. The CO$_2$ desorption experiment was conducted using the same absorption device, and only the bubbled gas was changed to pure N$_2$.

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