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Investigation of CO\textsubscript{2} Capture Efficiency and Mechanism in 2-Methylimidazole-Glycol Solution

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Abstract
Here, we report the fabrication of a stable CO\textsubscript{2} capture medium by dissolving 2-methylimidazole in glycol. It was found that 2-methylimidazole dissolved in glycol well, and their mixture showed good flowability. For single CO\textsubscript{2} absorption in the 10 wt\% 2-methylimidazole-glycol solution, the molar ratio between CO\textsubscript{2} and 2-methylimidazole molecules reached 0.79 at 293.15 K and 18.73 bar. It was supposed that an alkylcarbonate salt formed upon contact between 2-methylimidazole, glycol and CO\textsubscript{2}. This CO\textsubscript{2} absorption mechanism was further characterized by using the Fourier-transform infrared technology. For CO\textsubscript{2}/N\textsubscript{2} (20.65/79.36 mol\%) gas mixture separation in the 30 wt\% 2-methylimidazole-glycol solution, the equilibrium partial pressure of CO\textsubscript{2} in the gas phase could be decreased to as low as 0.10 bar with the selectivity of CO\textsubscript{2} over N\textsubscript{2} reaching 239 at 293.15 K and 4.55 bar. More importantly, the CO\textsubscript{2} uptake in 2-methylimidazole-glycol solution was reversible, CO\textsubscript{2} was readily desorbed from the solution through vacuuming at room temperature and with no apparent liquid loss. This work opens up the possibility of applying imidazole-alcohols mixtures to CO\textsubscript{2} capture.

Keywords: CO\textsubscript{2} capture; 2-methylimidazole-glycol solution; alkylcarbonate salt

1. Introduction
It is increasingly recognized that the accumulation of CO\textsubscript{2} in the atmosphere has resulted in many serious environmental problems. Therefore, the development of efficient methods for capturing CO\textsubscript{2} from industrial flue gases has become an important consideration for the energy and petrochemical industries in recent years. Three types of technology-absorption separation [1,2], adsorption
separation [3,4], and membrane separation [5,6] have been used for CO₂ capture to date. Among them, because of its easy operation, high capacity, and separation efficiency, CO₂ chemical absorption in aqueous amines is the most widely used so far. However, although the use of these aqueous amines is effective, there are some obvious drawbacks associated with them. For example, because of the high volatility of amines, it is difficult to keep most of the amine solutes in the solvent during the regeneration process; since CO₂ is strongly bound to amines in the amine solution, one needs to boil the solution to reverse the chemical bonding. The amine solution usually contains 70% water or higher. As a result, uptake of water into the gas stream causes intensive energy consumption, resulting in increased cost and corrosion problems.

In the past decade, room-temperature ionic liquids (RTILs) have been proposed as alternative or next-generation CO₂ absorption separation media [7-10]. As compared to traditional aqueous amines, RTILs show some unusual properties, such as extremely low vapor pressure, wide liquid temperature range, high thermal and chemical stability, and high CO₂ solubility [11]. CO₂ dissolution in most RTILs is a kind of physical absorption [12-16]. Sudhir et al. [16] measured the CO₂ solubility in 10 different imidazolium-based ionic liquids. They found that the CO₂ solubility in [bmim][Tf2N] reached over 0.7 mole fraction at 60 bar and that the solubility of CO₂ was strongly dependent on the choice of anion but not very dependent on the choice of cation. Cadena et al. [14] performed both experiments and molecular modeling studies to investigate the mechanism of high CO₂ solubility in imidazolium-based ionic liquids. They too found that anion had the greatest impact on the solubility of CO₂. To further improve the CO₂ absorption amount, amino-functionalized ionic were synthesized [17-20], which were found to be very effective. The molar uptake of CO₂ per mole these ILs could approached 0.5, which is the theoretical maximum for CO₂ sequestration as an ammonium carbamate salt. However, although the lack of an appreciable vapor pressure is a quality associated with ILs, it comes at the expense of high viscosity. The viscosities of virtually all RTILs are at least an order of magnitude lower than those of common organic solvents. For these functionalized RTILs, their unreacted states show much higher viscosities [19,20]. It is known that solvent viscosity is an important consideration for separation applications, because high viscosity typically correlates with low gas diffusion rates, which negatively impact both the mass and the heat transfer. Davis’s group [19] showed that their amine-tethered imidazolium IL took three hours to reach saturation for CO₂ absorption. Furthermore, Shannon et al.[21] stated some ILs will likely remain inherently more expensive to manufacture than conventional organic solvents because of the cost of starting materials, the number of reaction steps
needed, and, depending on the end use, the degree of purification required. In light of this, it is desirable to develop suitable absorbents that can facilitate the sequestration of CO\textsubscript{2} with low synthesis cost and good flow characteristics and without concurrent loss of the capture agent or solvent into the gas stream.

Recently, we [22] have proposed a kind of slurry system for CO\textsubscript{2} capture, in which zeolitic imidazolate framework-8 (ZIF-8), 2-methylimidazole, and glycol were mixed to form a flowable slurry. This mixture was then used for CO\textsubscript{2} capture. It was found that because of both the adsorption effect of ZIF-8 and absorption effect of the glycol solution, the slurry system showed promising high CO\textsubscript{2} selectivity. We also found that the addition of 2-methylimidazole into the ZIF-8/glycol slurry substantially increased the CO\textsubscript{2} absorption amount, although the mechanism of action of 2-methylimidazole in the slurry is not clear. Based on these preliminary findings, we here propose using a 2-methylimidazolate-glycol solution to perform CO\textsubscript{2} capture process. Intuitively, because of the high boiling points, low volatilities, and low cost of both glycol (boiling point: 197°C) and 2-methylimidazole (boiling point: 268°C), the 2-methylimidazolate-glycol solution may combine some advantages of both aqueous amine solutions (e.g. easy to synthesize, good flowability, and high CO\textsubscript{2} absorption amount) and ionic liquids (e.g. low vapor pressure) for CO\textsubscript{2} capture. As compared to the ZIF-8/glycol-2-methylimidazole slurry, although the adsorption effect of ZIF-8 is absent, the 2-methylimidazolate-glycol solution has a lower apparent viscosity.

This paper is organized as follows: First, measurement of the basal physical properties, including the solubility of 2-methylimidazole in glycol, and the density, pH, and viscosity of the 2-methylimidazolate-glycol solution is presented. Second, measurement of the CO\textsubscript{2} solubility in the 2-methylimidazolate-glycol solution, as well as the corresponding CO\textsubscript{2} absorption mechanism determined by using Fourier-transform infrared analysis technology is presented. Third, the CO\textsubscript{2} separation efficiency of the 2-methylimidazolate-glycol mixture is reported.

2. Experimental

2.1. Experimental apparatus

CO\textsubscript{2} capture. Both single CO\textsubscript{2} absorption and CO\textsubscript{2}/N\textsubscript{2} gas mixture separation experiments in this work were performed by using the experimental apparatus as schematically illustrated in Figure 1. The experimental apparatus was also used in some of our previous works [22,23]. The key parts of the apparatus are a transparent sapphire cell and a steel-made blind cell, both of which are installed in an air bath. The effective volume of the sapphire cell is 60 cm\textsuperscript{3} and that of the blind cell plus connected tubes is 112 cm\textsuperscript{3}. The maximum working pressures of these two cells are designed to be
20 MPa. To directly observe samples in the cell, a luminescence source of type LG100H is mounted on the outside of the cell. A secondary platinum resistance thermometer (type-pt100) is used as the temperature sensor. A calibrated Heise pressure gauge and differential pressure transducers are used to measure the system pressure. The uncertainties of pressure and temperature measurements are ±0.2 bar and ±0.1 K, respectively. Real-time reading of the system pressure is recorded by a computer.

![Schematic diagram of the experimental apparatus: resistance thermocouple detector (RTD), differential pressure transducer (DPT), and data acquisition system (DAS).](image)

**Physical properties determination.** The solubility of 2-methylimidazole in glycol was measured by the static equilibrium method in a thermostatic water bath. The pH was measured using a Phs-3c pH meter (Shanghai, China), the density with a 10 mL pycnometer, and the viscosity with a modified Cannon-Ubelohde suspended level capillary viscometers, 0.6 mm in diameter [24].

### 2.2. Materials
The materials used in this work included 2-methylimidazole, glycol and feed gases. 2-methylimidazole was purchased from Sigma-Aldrich. Glycol was purchased from Beijing Chemical Reagents Company, China. Analytical grade carbon dioxide (99.99%) and nitrogen (99.99%) were purchased from Beijing AP Beifen Gas Industry Company, China. The synthetic CO$_2$/N$_2$ (20.65/79.36 mol%) gas mixture was prepared in our own laboratory. A Hewlett-Packard gas chromatograph (HP 7890) was used to analyze the composition of the prepared gas mixture.
2.3. Experimental procedures for CO₂ capture

Before the experiment, the sapphire cell was dismounted from the apparatus, washed with distilled water and dried, and then loaded with a known quantity (20 mL) of 2-methylimidazole-glycol solution. After that, the cell was installed back into the apparatus. The system (sapphire cell + blind cell + tubes connecting two cells) was then purged through vacuuming. The blind cell and the sapphire cell were then disconnected by closing the top valve on the sapphire cell and a sufficient amount of feed gas was injected into the blind cell. After that, the air bath was set to the desired temperature. Once the temperature was reached and the pressure in the blind cell was stabilized, the pressure was recorded as the initial pressure, $P_0$. The top valve of the sapphire cell was opened slowly, letting the desired amount of feed gas flow into the sapphire cell from the blind cell. This valve was then closed and the magnetic stirrer around the sapphire cell was turned on. The pressure of the residual gas mixture in the blind cell was recorded as $P_1$. With the sorption of the injected gas by the solution, the system pressure in the sapphire cell decreased gradually. During each measurement, the pressure in the sapphire cell was recorded as a function of time. When the system pressure remained constant for at least one hour, it was considered that equilibrium was achieved. The equilibrium pressure of the sapphire cell was recorded as $P_E$. The magnetic stirrer was turned off. To measure the single CO₂ solubility in the absorption media, the CO₂ left in the blind cell was again released to the sapphire cell to reach a higher desired initial pressure than before, the magnetic stirrer was turned on again to obtain another CO₂ equilibrium absorption pressure, and so on. For the separation of CO₂ in the gas mixture, the equilibrium gas phase needed to be sampled under constant pressure by use of a hand pump. The obtained gas sample was analyzed by a HP 7890 gas chromatograph. The volume of the absorption liquid in the sapphire cell was calculated by measuring its height. The inner radius of the sapphire cell is known to be 1.27 cm. The amount of each gas species absorbed in the measured sample was determined through mass balance as described below.

2.4. Data processing

The total number of moles of gases ($n_t$) that was injected into the sapphire cell was calculated using the following equation:

$$ n_t = \frac{P_0 \times V_i}{Z_0 \times R \times T} - \frac{P_1 \times V_i}{Z_i \times R \times T} $$

(1)

where $T$ is the system temperature, $P_0$ is the initial pressure in the blind cell, $P_1$ is the equilibrium pressure of the blind cell after injecting gases into the sapphire cell, $V_i$ is the total volume of the
blind cell plus tubes connecting to it, and $R$ is the gas constant. Compressibility factors $Z_0$ and $Z_1$ were calculated using the Benedict-Webb-Rubin-Starling equation of state. The total gas amount ($n_E$) in the equilibrium gas phase of the sapphire cell after absorption equilibrium was determined using:

$$n_E = \frac{P_E \times V_E}{Z_E \times R \times T}$$

(2)

where $P_E$ is the equilibrium pressure of the sapphire cell and $Z_E$ is the compressibility factor corresponding to $T$, $P_E$, and the gas composition. $V_E$ is the volume of equilibrium gas phase in the sapphire cell at the end of each experimental run.

For single CO$_2$ absorption, both the mole percent ($x$) of CO$_2$ in the liquid phase and the mole ratio ($\alpha$) of CO$_2$ to 2-methylimidazole (mIm) were used to indicate the CO$_2$ absorption ability of the 2-methylimidazole-glycol solution.

$$x = \frac{n_{CO2}}{n_{CO2} + n_{mIm} + n_{glycol}}$$

(3)

$$\alpha = \frac{n_{CO2}}{n_{mIm}}$$

(4)

$$n_{CO2} = n_{CO2} - P_E \times m_w / H$$

(5)

where $n_{CO2}$ is the total uptake of CO$_2$ in the solution, $n_{mIm}$ and $n_{glycol}$ are respectively the molar number of 2-methylimidazole and glycol in the fresh solution, $m_w$ (g) is the glycol mass used, and $H$ [(g bar)/mmol] is the Henry constant of CO$_2$ in glycol, which is equal to 21.6 (g bar)/mmol at 293.15 K, as obtained in our previous work [22].

For separation of the CO$_2$/N$_2$ gas mixture in the 2-methylimidazole-glycol solution, the selectivity ($S$) of CO$_2$ over N$_2$ was used to indicate the CO$_2$ separation efficiency of the solution:

$$S = \frac{x_1 / y_1}{x_2 / y_2}$$

(6)

where $x_1$ and $x_2$ are the mole percents of CO$_2$ and N$_2$, respectively, in the absorbed phase and $y_1$ and $y_2$ are the mole percents of CO$_2$ and N$_2$, respectively, in the equilibrium gas phase.

Accordingly, the apparent mole percents of CO$_2$ ($x_1$) and N$_2$ ($x_2$) in the equilibrium liquid phase can be obtained by the following formulas:

$$x_i = \frac{n_i}{n_1 + n_2}$$

(7)
The total uptake of CO$_2$ ($n_1$) and N$_2$ ($n_2$) in solution was calculated as follows:

\[ x_2 = \frac{n_2}{n_1 + n_2} \]  

(8)

where $x_2$ is the mole percent of CO$_2$ in solution and $n_1$ and $n_2$ are the molar amounts of CO$_2$ and N$_2$, respectively. In the synthetic gas, $z_1$ and $z_2$ are the mole percent of CO$_2$ and N$_2$, respectively, and $y_1$ and $y_2$ are the mole percent of CO$_2$ and N$_2$, respectively, in the equilibrium gas phase.

3. Experimental results and discussion

3.1. Physical properties of 2-methylimidazole-glycol solution

The solubility of 2-methylimidazole in glycol at 293.15, 298.15 and 303.15 K are reported in Table 1. As can be seen in the Table 1, the solubility of 2-methylimidazole in glycol was 35.1 mol% at 293.15 K, and it quickly increased to 42.2 mol% at 303.15 K, demonstrating that 2-methylimidazole easily dissolved in glycol, especially at high temperatures. The corresponding solubility in weight percent changed from 41.7 wt% to 49.1 wt% in the studied temperature range.

<table>
<thead>
<tr>
<th>Solubility</th>
<th>T (K)</th>
<th>293.15</th>
<th>298.15</th>
<th>303.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole percent (mol%)</td>
<td>35.1</td>
<td>38.8</td>
<td>42.2</td>
<td></td>
</tr>
<tr>
<td>weight percent (wt%)</td>
<td>41.7</td>
<td>45.6</td>
<td>49.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 summarizes both the density and the pH value of the 2-methylimidazole-glycol solution at 303.15 K and at four different weight percents ($m_t$) of 2-methylimidazole. For the density measurement, it was found that because the density of solid 2-methylimidazole crystals (1.03 g/cm$^3$) is lower than that of glycol (1.113 g/cm$^3$), the solution density decreased linearly with increasing 2-methylimidazole concentration. For example, at $m_t = 40$ wt%, the solution density decreased to 1.077 g/cm$^3$ from the 1.113 g/cm$^3$ of pure glycol. As concerns pH, the pH of pure glycol is 7.79. After adding 10 wt% 2-methylimidazole, the pH of the solution sharply increased to 10.12. However, unlike to the change of density, further increases of $m_t$ increased the pH of the solution only slightly. Higher pH values usually indicate stronger absorption ability of the absorbent for acid gas components; thus, the results show that the 2-methylimidazole-glycol solution would be more suitable for CO$_2$ capture than pure glycol.
Table 2
Density and pH of 2-methylimidazole-glycol solution versus 2-methylimidazole weight percent \( (m_f) \) at 303.15 K and atmospheric pressure

<table>
<thead>
<tr>
<th>( m_f )</th>
<th>0</th>
<th>10 wt%</th>
<th>20 wt%</th>
<th>30 wt%</th>
<th>40 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>density</td>
<td>1.113</td>
<td>1.104</td>
<td>1.095</td>
<td>1.086</td>
<td>1.077</td>
</tr>
<tr>
<td>pH</td>
<td>7.79</td>
<td>10.12</td>
<td>10.39</td>
<td>10.71</td>
<td>10.93</td>
</tr>
</tbody>
</table>

As mentioned in the introduction, viscosity is an important property for CO\(_2\) absorbents because a lower viscosity usually correlates to a higher gas-liquid mass transfer rate and lower transmission cost during circulation in the absorption column. Table 3 presents the experimental viscosity \( (\eta) \) of the 2-methylimidazole-glycol solution at four temperatures (293.15, 303.15, 313.15 and 323.15 K) and six 2-methylimidazole percents \( (m_f = 0, 10, 20, 30 \text{ and } 40 \text{ wt\%}) \) at atmospheric pressure. The viscosity of pure glycol at 293.15 K is 19.9 mPa·s, which is the same as that reported by others [25]. Regarding the 2-methylimidazole-glycol solution, the addition of 2-methylimidazole moderately increased its viscosity, reaching only 27.4 mPa·s at 303.15 K at the maximum \( m_f \) (40 wt\%) studied here. This viscosity is much lower than the viscosities of most RTILs reported in the literature.\(^7\) Furthermore, the viscosity of the solution decreased rapidly with increasing of temperature. As a result, the solution easily circulated in the common industrial absorption column.

Table 3
Viscosities of 2-methylimidazole-glycol solution versus temperature \( (T) \) and 2-methylimidazole weight percent \( (m_f) \) in it at atmospheric pressure

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( m_f = 0 )</th>
<th>( m_f = 5 \text{ wt%} )</th>
<th>( m_f = 10 \text{ wt%} )</th>
<th>( m_f = 20 \text{ wt%} )</th>
<th>( m_f = 30 \text{ wt%} )</th>
<th>( m_f = 40 \text{ wt%} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>19.9</td>
<td>14.8</td>
<td>16.1</td>
<td>18.8</td>
<td>22.6</td>
<td>47.5</td>
</tr>
<tr>
<td>303.15</td>
<td>13.2</td>
<td>14.8</td>
<td>16.1</td>
<td>18.8</td>
<td>22.6</td>
<td>27.4</td>
</tr>
<tr>
<td>313.15</td>
<td>9.5</td>
<td>14.8</td>
<td>16.1</td>
<td>18.8</td>
<td>22.6</td>
<td>17.6</td>
</tr>
<tr>
<td>323.15</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.4</td>
</tr>
</tbody>
</table>

After that, we performed a series of pure CO\(_2\) dissolution and CO\(_2\)/N\(_2\) gas mixture separation experiments in the 2-methylimidazole-glycol solution to investigate the CO\(_2\) capture efficiency of the solution. The corresponding experimental results are summarized in Tables 4-7 and are shown in Figures 2-5.

3.2. CO\(_2\) solubility in 2-methylimidazole-glycol solution

Table 4 summarizes the solubility data of CO\(_2\) in 2-methylimidazole-glycol solutions at 293.15 K and three weight percents of 2-methylimidazole (10, 30 and 40 wt\%). To compare the results with those of commonly employed aqueous amines, CO\(_2\) solubility in a 30 wt\% aqueous
monoethanolamine (MEA) solution was also measured. The experimental results are presented in Table 4, as well as in Figure 2. The solubility \(x\) of CO\(_2\) in the 2-methylimidazole-glycol solution increased with increasing pressure and \(m_f\) of 2-methylimidazole. For example, when \(m_f\) increased from 10 wt% to 30 wt% at 10 bar, the CO\(_2\) solubility in the solution increases from \(\sim 7.5\) mol% to \(\sim 11.5\) mol%. However, at low pressures \((\leq 5\) bar\), a further increase of \(m_f\) from 30 wt% to 40 wt% did not lead to an apparent change of \(x\). We think the reason for this is that when \(m_f\) reached 30 wt% or higher, the relatively high viscosity of the solution decreased the dissolution of CO\(_2\). In other words, increasing the number of 2-methylimidazole molecules at both the gas-liquid surface and in the bulk phase also hindered the dissolution of CO\(_2\) in the liquid at these low pressures. Increasing the pressure further served to offset this inhibition because the solubility of CO\(_2\) in the 40 wt% 2-methylimidazole-glycol solution was higher than that in the 30 wt% 2-methylimidazole-glycol solution. It is interesting to note that for the 30 wt% 2-methylimidazole-glycol solution at 1.25 bar, which is only slightly higher than atmospheric pressure, the CO\(_2\) solubility in the solution reached 4.59 mol%, which is higher than the CO\(_2\) solubility obtained in most RTILs. These results suggest that the 2-methylimidazole-glycol solution may be more suitable for CO\(_2\) capture than these ILs under some practical conditions with low CO\(_2\) partial pressures, such as the capture of CO\(_2\) from flue gas or biogas. However, the CO\(_2\) solubility in these ILs increased to the same level or even higher than that in the 2-methylimidazole-glycol solution at pressures higher than 10 bar. As compared to the 30 wt% MEA aqueous solution, the solubility of CO\(_2\) in the 2-methylimidazole-glycol solution at low pressures was lower, whereas the CO\(_2\) solubility in the 2-methylimidazole-glycol solution increased with increasing pressure much faster than that in the MEA solution. At pressures higher than 6 bar, the solubility of CO\(_2\) in the 2-methylimidazole-glycol solution was higher. More importantly, problems such as corrosion and solvent or solute loss during the regeneration process for absorbents could be substantially weakened or even eliminated when using the 2-methylimidazole-glycol solution as compared to aqueous amines because of the much lower volatility of the former.

Table 4

<table>
<thead>
<tr>
<th>(m_f) (wt%)</th>
<th>(P) (bar)</th>
<th>(x) (mol%)</th>
<th>(\alpha) (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylimidazole-glycol solutions</td>
<td>10</td>
<td>3.30</td>
<td>4.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.33</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.20</td>
<td>6.07</td>
</tr>
</tbody>
</table>
Table 4 also presents the molar ratios ($\alpha$) of CO$_2$ to 2-methylimidazole dissolved in the solution at different pressures and 2-methylimidazole contents. The ratio increases with increasing pressure but decreased with increasing 2-methylimidazole weight percent in the solution. For $m_t = 10$ wt% at 18.73 bar, the mole ratio between CO$_2$ and 2-methylimidazole reached 0.79, which is much higher than the theoretical maximum of 0.5 for CO$_2$ sequestration as an ammonium carbamate salt in amino-functionalized ILs and some aqueous amines [19,26-28]. The high CO$_2$ solubility in the 2-methylimidazole-glycol solution should not be attributed to the formation of ammonium carbamate salt as we guessed before [22]. Instead, it is more likely that the system studied here forms a so-called “switchable organic liquid” [29-32], in which an alcohol and an amidine or guanidine base, triggered by CO$_2$, chemically binds with CO$_2$ to form an amidinium or guanidinium alkylcarbonate salt. Therefore, we propose the possible reaction of CO$_2$ absorption by the 2-methylimidazole-glycol solution shown in Schematic 1.
Schematic 1. Proposed CO$_2$ absorption mechanism in 2-methylimidazole-glycol solution.

In this reaction, a certain 2-methylimidazole alkylcarbonate salt (or ionic liquid) is formed in the presence of CO$_2$, glycol, and 2-methylimidazole, in which CO$_2$ acts as a “switch” to elicit this change. It should be noted that the formed 2-methylimidazole alkylcarbonate salt shown in Schematic 1 differs from common ionic liquids because it is only an ionic liquid after the CO$_2$ is chemically bound. It is also obvious from Schematic 1 that if enough pressure is applied, the reaction of CO$_2$ with 2-methylimidazole should terminate at 1:1 stoichiometry. Table 4 shows that the molar ratio of CO$_2$ to 2-methylimidazole decreases with increasing 2-methylimidazole weight percent in the solution. The possible reason for this is that the formation of 2-methylimidazole alkylcarbonate salt increased the viscosity of the solution to a certain extent, resulting in the reduction of CO$_2$ dissociation in the solution. As a result, a relatively low 2-methylimidazole concentration may be more suitable for the reaction between 2-methylimidazole, glycol, and CO$_2$. However, a lower 2-methylimidazole content also means a lower CO$_2$ absorption amount in the solution, as shown in Table 4. Therefore, taking into account both the efficiency and CO$_2$ absorption capacity, we think that 30 wt% is a suitable concentration for 2-methylimidazole in a 2-methylimidazole-glycol solution to be used for CO$_2$ capture.
Then, the influence of temperature on the CO$_2$ solubility measurement in the 2-methylimidazole-glycol solution was studied. In this group of experiments, the weight percent of 2-methylimidazole in the solution was set to 40 wt%. Generally, as shown in Table 5, the solubility of CO$_2$ in the 2-methylimidazole-glycol solution decreased with decreasing temperature, which is reasonable because more CO$_2$ was absorbed by glycol and reacted with glycol and 2-methylimidazole, converting to the 2-methylimidazole alkylcarbonate salt at low temperature.

**Table 5**

CO$_2$ solubility in 2-methylimidazole-glycol solution (40 wt% 2-methylimidazole) at three different temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$x$ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>2.19</td>
<td>5.83</td>
</tr>
<tr>
<td></td>
<td>3.34</td>
<td>7.58</td>
</tr>
<tr>
<td></td>
<td>5.25</td>
<td>9.82</td>
</tr>
<tr>
<td></td>
<td>6.87</td>
<td>11.40</td>
</tr>
<tr>
<td></td>
<td>8.88</td>
<td>12.82</td>
</tr>
<tr>
<td></td>
<td>10.54</td>
<td>14.01</td>
</tr>
<tr>
<td></td>
<td>12.33</td>
<td>15.05</td>
</tr>
<tr>
<td>303.15</td>
<td>2.23</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>3.42</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>4.98</td>
<td>7.84</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>10.12</td>
</tr>
</tbody>
</table>
In order to investigate the validity of the proposed CO\textsubscript{2} absorption mechanism shown by Schematic 1, we measured the Fourier-transform infrared (FT-IR) spectra for both the neat 2-methylimidazole-glycol solution and the solution after treatment with CO\textsubscript{2}. As shown in Figure 3, upon exposure to CO\textsubscript{2}, three new peaks at 1239 cm\textsuperscript{-1}, 1637 cm\textsuperscript{-1} and 2335 cm\textsuperscript{-1} emerged for the CO\textsubscript{2}-2-methylimidazole-glycol mixture. The peak at 1637 cm\textsuperscript{-1} is consistent with the formation of a new C=O group [33]. The new peak at 1239 cm\textsuperscript{-1} is due to the symmetric stretching vibration of the -C-O-C- group [34]. The peak at 2335 cm\textsuperscript{-1} corresponds to the asymmetric and bending modes of the CO\textsubscript{2} molecules [35]. The existence of free CO\textsubscript{2} molecules in the solution is attributed to the physical dissolution of CO\textsubscript{2} in glycol that has not reacted with 2-methylimidazole and CO\textsubscript{2}. These results suggest that CO\textsubscript{2} dissolution in the 2-methylimidazole-glycol solution includes both physical and chemical absorption processes. Moreover, with the formation of 2-methylimidazole alkylcarbonate salt, the intensity of the broad band between 3200 and 3400 cm\textsuperscript{-1}, which corresponds to the hydrogen bonds formed between glycol molecules decreases because of the reduction in single glycol content. In short, the FT-IR analysis results are in good agreement with the proposed CO\textsubscript{2} absorption mechanism.
3.3. CO₂ separation efficiency of 2-methylimidazole-glycol solution

Because CO₂ showed high solubility in the 2-methylimidazole-glycol solution, further separation experiments were carried out for a simulated flue gas (CO₂/N₂, 20.65/79.35 mol%) using the 2-methylimidazole-glycol solution. Table 6 shows the separation results for this CO₂/N₂ gas mixture in the 30 wt% 2-methylimidazole-glycol solution, where \( P₀ \) and \( Pₑ \) are respectively the initial and equilibrium pressures in the sapphire cell and \( Pₑ-CO₂ \) is the partial pressure of CO₂ in the equilibrium gas phase. \( y₁ \) and \( x₁ \) are the mole percents of CO₂ in the equilibrium gas phase and liquid phase, respectively. \( S \) is the selectivity of CO₂ over N₂. As can be seen, the selectivity (\( S \)) of CO₂ over N₂ decreases with increasing temperature and pressure. For the experiment at 4.55 bar and 293.15 K, after a single equilibrium separation stage, the mole percent of CO₂ in the gas phase decreased from 20.65 mol% in the feed gas to as low as 2.32 mol%. The CO₂ selectivity reached 239, a value that is much higher than that for most absorbents reported in the literature. More importantly, the CO₂ partial pressure in the gas phase was only 0.10 bar, much lower than the partial pressures of CO₂ in the common CO₂ containing gas mixtures. Even at a \( Pₑ \) of 18.06 bar at 313.15 K, \( S \) was still as high as 112. In short, the high selectivity over a wide pressure range and the low CO₂ equilibrium partial pressures demonstrate that the 2-methylimidazole-glycol solution is suitable for capturing CO₂ from different kinds of feed gases such as flue gas (CO₂/N₂, ~1 bar), biogas (CO₂/CH₄, ~1 bar), and
integrated gasification combined cycle gas (CO$_2$/H$_2$, 3~5 MPa). At the same time, we think other imidazole materials containing –NH bond, such as imidazole, 4-methylimidazole, benzimidazole, and so on, should also be suitable for mixing with glycol to capture CO$_2$ from gas mixtures.

Table 6
CO$_2$/N$_2$ (20.65/79.35 mol%) gas mixture separation results in the 30 wt% 2-methylimidazole-glycol solution at different pressures and temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$P_0$ (bar)</th>
<th>$P_E$ (bar)</th>
<th>$P_{E-CO2}$ (bar)</th>
<th>$y_1$ (mol%)</th>
<th>$x_1$ (mol%)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>5.83</td>
<td>4.55</td>
<td>0.10</td>
<td>2.32</td>
<td>85.08</td>
<td>239</td>
</tr>
<tr>
<td>303.15</td>
<td>7.71</td>
<td>5.99</td>
<td>0.14</td>
<td>2.37</td>
<td>83.94</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>16.82</td>
<td>13.34</td>
<td>0.41</td>
<td>3.05</td>
<td>84.87</td>
<td>178</td>
</tr>
<tr>
<td>313.15</td>
<td>6.72</td>
<td>5.23</td>
<td>0.14</td>
<td>2.68</td>
<td>83.73</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>11.76</td>
<td>9.22</td>
<td>0.27</td>
<td>2.88</td>
<td>83.93</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>16.70</td>
<td>13.48</td>
<td>0.46</td>
<td>3.39</td>
<td>85.23</td>
<td>164</td>
</tr>
</tbody>
</table>

Figure 4 shows the kinetics of the CO$_2$/N$_2$ (20.65/79.36 mol%) gas mixture separation processes in the 30 wt% 2-methylimidazole-glycol solution at 303.15 K. Regardless of the initial pressures ($P_0$) in the reactor, all these experiments can reached nearly equilibrium pressure within approximately 10 min, showing the high CO$_2$ capture rate of the 2-methylimidazole-glycol solution from gas mixtures.
Fig. 4. Kinetics of CO$_2$/N$_2$ gas mixture separation processes in the 30 wt% 2-methylimidazole-glycol solution at 303.15 K with different initial pressures ($P_0$) in the sapphire cell.

Essential to any CO$_2$ capture media is the energy required for gas release. Here, it is important to note that all measurements for the CO$_2$/N$_2$ (20.65/79.36 mol%) gas mixture separation equilibrium listed in Table 6 were performed using the same solution through cycles of sorption/desorption (that is, vacuum applied at room temperature for desorption). We observed no remarkable loss of the volume and separation ability of the solution after nine cycles, demonstrating the high stability and reusability of the 2-methylimidazole-glycol solution. Figure 5 further presents the morphologies of the 30 wt% 2-methylimidazole-glycol solution during CO$_2$ capture processes at 303.15 K. Both the fresh and the CO$_2$ absorbed 2-methylimidazole-glycol solutions are transparent, showing that the 2-methylimidazole alkylcarbonate salt formed during CO$_2$ capture process was well dissolved in the glycol. Moreover, it is important to note that although the formation of the 2-methylimidazole alkylcarbonate salt might have increased the viscosity of the absorbent, after separation equilibrium, the stirrer at the bottom of the sapphire cell easily started with the up-and-down motion of the magnetic around the sapphire cell, showing that the equilibrium solution maintained acceptable flowability. Figure 5c shows the regeneration process of the CO$_2$ captured 2-methylimidazole-glycol solution. When the pressure in the sapphire cell was decreased to subatmospheric pressure, the CO$_2$ in the solution desorbed quickly. It was found that with stirring and under vacuum (~0.2 bar), the solution could be regenerated in less than half an hour at room temperature. Meanwhile,
based on the CO₂ absorption results under different temperatures listed in Table 6, we calculated that the CO₂ absorption enthalpy in the 2-methylimidazole-glycol solution was only approximately 32 kJ mol⁻¹ (Figure 6), which is much lower than that in typical chemical absorption or chemical adsorption processes [36,37]. This value also shows the easily regeneration phenomenon of the solution.

![Fig. 5. Morphologies of the 30 wt% 2-methylimidazole-glycol solution during CO₂ capture at 293.15 K: (a) fresh 2-methylimidazole-glycol solution, (b) 2-methylimidazole-glycol solution after separation equilibrium for the CO₂/N₂ (20.65/79.36 mol%) gas mixture, and (c) regeneration process for CO₂ captured 2-methylimidazole-glycol solution through evacuation.](image)

![ΔH vs n](image)
Fig. 6. Absorption enthalpy of CO\textsubscript{2} in 2-methylimidazole-glycol solution.

Finally, the effect of the 2-methylimidazole content ($m_f$) on the CO\textsubscript{2} separation efficiency of the 2-methylimidazole-glycol solution was also investigated. As shown in Table 7, a relatively higher $m_f$ corresponds to a lower CO\textsubscript{2} partial pressure in the equilibrium gas phase and higher CO\textsubscript{2} selectivity ($S$). However, it should be noted that a higher 2-methylimidazole content also means higher viscosity for both the fresh and CO\textsubscript{2}-captured 2-methylimidazole-glycol solutions. Thus, taking both the CO\textsubscript{2} separation efficiency and flow behavior into consideration, the weight percent of the 2-methylimidazole in the solution should not be more than 30\% in practical use.

Table 7

CO\textsubscript{2}/N\textsubscript{2} (20.65/79.35 mol\%) gas mixture separation results in different concentration of 2-methylimidazole-glycol solution at 293.15 K

<table>
<thead>
<tr>
<th>$m_f$ (wt%)</th>
<th>$P_0$ (MPa)</th>
<th>$P_E$ (MPa)</th>
<th>$P_{E-CO2}$ (MPa)</th>
<th>$y_1$ (mol%)</th>
<th>$x_1$ (mol%)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>16.62</td>
<td>14.15</td>
<td>1.32</td>
<td>9.37</td>
<td>80.76</td>
<td>41</td>
</tr>
<tr>
<td>15</td>
<td>16.72</td>
<td>13.51</td>
<td>0.59</td>
<td>4.33</td>
<td>86.02</td>
<td>136</td>
</tr>
<tr>
<td>30</td>
<td>16.82</td>
<td>13.34</td>
<td>0.41</td>
<td>3.05</td>
<td>84.87</td>
<td>178</td>
</tr>
<tr>
<td>40</td>
<td>17.23</td>
<td>13.54</td>
<td>0.39</td>
<td>2.88</td>
<td>84.88</td>
<td>189</td>
</tr>
</tbody>
</table>

5. Conclusions

In this work, we propose to use a 2-methylimidazole-glycol solution for CO\textsubscript{2} capture. First, some basic physical properties, including the solubility of 2-methylimidazole in glycol and the density, pH, and viscosity of the 2-methylimidazole-glycol solution were measured. It was found that 2-methylimidazole crystals dissolved well in glycol, with a solubility of 42 mol\% at 303.15 K. The density of the 2-methylimidazole-glycol solution decreased and its pH and viscosity increased with increasing 2-methylimidazole concentration. Then, the solubility of CO\textsubscript{2} in the 2-methylimidazole-glycol solution was measured. The experimental results showed that the CO\textsubscript{2} solubility increased with increasing pressure and increasing 2-methylimidazole weight percent. For the 10 wt\% 2-methylimidazole-glycol solution at 293.15 K and 18.73 bar, the molar ratio between CO\textsubscript{2} and the 2-methylimidazole molecules reached 0.79 after absorption equilibrium. Based on these results, a CO\textsubscript{2} absorption mechanism in the solution was proposed, in which CO\textsubscript{2} is bound with 2-methylimidazole and glycol to form an alkylcarbonate salt. In this reaction, CO\textsubscript{2} acts as a “switch”
to elicit the reaction. Further confirmation of the proposed CO$_2$ absorption mechanism was made using FT-IR analysis. Finally, a group of separation experiments for a CO$_2$/N$_2$ (20.65/79.36 mol%) gas mixture in a 2-methylimidazole-glycol solution were performed to investigate the CO$_2$ separation efficiency of the solution. The equilibrium separation results showed that the maximum selectivity of CO$_2$ over N$_2$ reached 239 at 293.15 K and 4.55 bar; under these conditions, the partial pressure of CO$_2$ in the gas phase was reduced to as low as 0.10 bar. The most suitable 2-methylimidazole concentration in 2-methylimidazole-glycol solution was determined to be 30 wt%. More importantly, CO$_2$-capturing 2-methylimidazole-glycol solutions maintained good flowability and could be easily regenerated through vacuuming at room temperature. Because both glycol and 2-methylimidazole have high boiling points, low volatilities, and are relatively inexpensive, the 2-methylimidazole-glycol solution should be well applicable for CO$_2$ capture. Furthermore, considering the diversities of both imidazoles and alcohols, it is expected that the experimental results obtained in this work would promote application of imidazole-alcohol mixtures in CO$_2$ capture research.

Acknowledgements

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References


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**Highlights**

1. 2-methylimidazole-glycol solution is proposed to capture CO$_2$;
2. CO$_2$ solubility in 2-methylimidazole-glycol solution was measured;
3. CO$_2$ separation efficiency in 2-methylimidazole-glycol was investigated;
4. CO$_2$ capture mechanism was determined through Fourier-transform infrared technology.