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Reversible carbon dioxide capture at high temperatures by
tetraethylenepentamine acetic acid and polyethylene glycol mixtures with
high capacity and low viscosity

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ABSTRACT

Ionic liquids (ILs) are investigated in many studies to capture CO₂ in recent years.
However, almost all of these studies carried out the absorption of CO₂ by ILs at relatively low
temperatures (lower than 333.15K or even around the room temperature). Besides, the
viscosity of ILs increases dramatically after absorbing CO₂ which could reduce the absorption
efficiency significantly. Reversible and efficient absorption of CO₂ at high temperatures was
investigated by IL of tetraethylenepentamine acetic acid ([TEPA]Ac) and polyethylene glycol
200 (PEG-200) mixtures with low viscosity. The results showed that the absorption capacity

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of [TEPA]Ac/PEG-200 mixtures achieved to 1.24 mol CO$_2$ per mole [TEPA]Ac at 353.15 K at ambient pressure (1.01 bar). The mixtures could be easily regenerated by bubbling dried N$_2$ through them. The addition of PEG-200 in the [TEPA]Ac could increase the efficiency of absorption and desorption significantly. Furthermore, the solubility data of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures at T = (353.15, 368.15, 383.15, and 398.15) K under different pressures were measured and the solution enthalpy (ΔH$_{sol}$) and solution entropy (ΔS$_{sol}$) were calculated. Under all the conditions, the negative value of ΔH$_{sol}$ indicated that the capture process is exothermic. The process of CO$_2$ capture described that using [TEPA]Ac/PEG-200 mixtures is a promising approach for CO$_2$ absorption with high reversibility and excellent absorption property at a relatively high temperature.

**Keywords:** Carbon capture, Ionic liquid, Tetraethylenepentamine acetic acid, Polyethylene glycol, High temperature, High capacity

1. **Introduction**

The emission of CO$_2$ from fossil fuel combustion causes serious effect to the environment and contributes to global warming and ocean acidification. Therefore, the concept of carbon capture and storage (CCS) has drawn considerable attention by the researchers during these years [1, 2]. The carbon capture technologies such as absorption, adsorption, and membrane gas separation technologies are developed and applied worldwide [3-8]. Physical absorbents, such as monoethanolamine (MEA), can absorb CO$_2$ at high partial pressures and low temperatures, which have been used industrially for many years. However,
large energy consumption was consumed and partial decomposition occurred during regeneration process. Adsorption materials, such as carbon-based sorbents (e.g. carbon molecular sieves) and metal oxides (e.g. CaO, Li$_2$ZrO$_3$) have been used for CO$_2$ capture at high temperature (above 300°C). For example, the CaO can capture CO$_2$ at 600-800°C with the mole ratio approach of 1.0 and regenerated at 800-850°C. In addition, membrane is also a type of promising utilization of reversible material for CO$_2$ capture. The advantages of membrane absorption material are selective extraction of CO$_2$ from mixed gas streams and flexibility in their possible configurations in industrial plants. However, a common disadvantage of the membrane materials is their lack of stability under the application environment [7-10]. Therefore, seeking promising alternatives with low energy consumption and high stability to these solvents is desirable.

Ionic liquid (IL) is a promising material regarded as a kind of environmentally-friendly solvent which processes some superior properties, for example, wide liquid temperature range, low vapor pressure, high thermal and chemical stability, and excellent solvent power [11, 12]. Recently, there is a significant progress in the application of IL for CO$_2$ capturing.

Blanchard et al. [13] firstly reported that CO$_2$ could be absorbed by 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF$_6$] effectively, but the IL of [BMIM][PF$_6$] could not be dissolved in CO$_2$. After that, many researchers were engaged in the study of CO$_2$ capturing with ionic liquid [14, 15]. Bates et al. [16] synthesized a kind of IL by inducing a primary amine moiety and tetrafluoroborate anion to the structure of imidazolium cation and studied its property related to CO$_2$ absorption. Their results showed that the IL had a good effect on carbon absorption and molar absorption ratio of CO$_2$ to IL.
could approach 0.5. Galan Sanchez et al. [17] studied the absorption of CO$_2$ in different imidazolium-based ILs. They found out that the efficiency of CO$_2$ absorption increased significantly by attaching basic groups to the structure of the ILs. Gurkan et al. [18] reported that equimolar amount of CO$_2$ could be absorbed by the IL with amino acids anion. Zhang et al. [19] synthesized the phosphonium-based ILs with various amino acid anions for carbon capture. When the ILs were saturated with CO$_2$, the mole ratio of CO$_2$ to IL approached to 1.0.

Although ILs have many attractive superiorities for CO$_2$ capturing, they still have some drawbacks that need to be modified, such as promoting the absorption capacity and decreasing the viscosity [20, 21]. Furthermore, the capacity of CO$_2$ absorption by the present ILs declined dramatically when temperature elevated to 353.15 K [22]. Thus, their application for the CO$_2$ capture and storage was limited at low temperatures, being less than 333.15 K or even at room temperature [23, 24]. However, temperature of the flue gas is usually higher than room temperature and ranges from 353.15 K to 393.15 K. Therefore, designing new absorbents to capture CO$_2$ at higher temperatures (from 353.15 K to 393.15 K), with high absorption capacity, and high efficiency is required.

In the present work, a new type of IL-based adsorbent of tetraethylenepentamine acid ([TEPA]Ac) and [TEPA]Ac in polyethylene glycol (PEG) with average molecular weight of 200 g/mol (PEG-200) was studied for carbon capture. PEG-200 was mainly selected as a solvent to dissolve [TEPA]Ac in order to decrease the viscosity of the IL after absorbing CO$_2$. Also, PEG has other important advantages, such as nontoxic, biodegradable, nonvolatile, and cheap [25, 26]. In addition, the solubility of CO$_2$ in [TEPA]Ac/PEG-200 mixture at four
temperatures under different pressures was also measured and the thermodynamic parameters were calculated by the thermodynamics theory and solubility data.

2. Materials and Methods

2.1 Materials

CO$_2$ (99.999%) and N$_2$ (99.999%) were provided from Messer Gases Co. Ltd. (Guangzhou, China). Tetraethylenepentamine (TEPA) ($\geq$ 99%) was supplied by Damao chemical reagent Co. Ltd. (Tianjin, China). Acetic acid (Ac) ($\geq$ 99.5%) and polyethylene glycol (PEG-200, $\geq$ 99.5%) were purchased from Runjie chemical reagent Co. Ltd. (Tianjin, China).


[TEPA]Ac was synthesized in following reaction:

\[
\text{H}_3\text{C COOH} + \text{NH}_2\text{NCH}_2\text{NCH}_2\text{NCH}_2\text{N} + \text{NH}_2\text{CH}_2\text{COOH} \rightarrow \text{H}_3\text{C COOH} + \text{NH}_2\text{NCH}_2\text{NCH}_2\text{N} + \text{NH}_2\text{CH}_2\text{COOH}
\]

The procedure included following steps: 1) 0.5 mol of TEPA and 150 mL of water were added into a 500 mL three-necked flask which was placed in an ice-water bath with a magnetic stirrer; 2) 0.5 mol of Ac was added dropwise from a pressure funnel to the flask over about 1.0 h. Then the reaction continued for 8 h at 298.15 K. 3) After that, the water was removed by a rotary evaporator and being dried under vacuum at 353.15 K for more than 48 h.
before use. After the drying process, the fractions of water were less than 0.5% which were determined by Karl Fischer titration.

The mixtures of [TEPA]Ac/PEG-200 were prepared with mass ratio of [TEPA]Ac to PEG-200 at 1:1, 1:2 and 1:3 by an analytical balance (AR224CN, OHAUS) with a precision of 0.1 mg. After mixing, the solutions were kept in the vacuum oven at 353.15 K for 48 hours to remove the volatile impurities and possible traces of water and then stored in a desiccator.

2.3 Absorption and desorption of CO₂

The process of absorption and desorption of CO₂ was carried out at ambient pressure. Figure 1 shows an experimental device for absorption and desorption of CO₂ by [TEPA]Ac. The temperature of an oil bath was controlled by a thermo controller. About 5.0 g of the [TEPA]Ac/PEG-200 mixture was loaded in the glass tube which was partly immersed in the oil bath at desired temperature, and then CO₂ was bubbled through the absorbent at the rate of 100 cm³/min which was controlled by the gas rotameter.

![Fig. 1 Experimental device for CO₂ absorption and desorption by [TEPA]Ac: ① Cylinder](image-url)
filled with pure \( \text{N}_2 \); ② Cylinder filled with pure \( \text{CO}_2 \); ③ Valves; ④ Flow meters; ⑤ Glass tube filled with [TEPA]Ac or [TEPA]Ac/PEG-200; ⑥ Oil baths; ⑦ NaOH aqueous solution for absorbing the exhaust \( \text{CO}_2 \).

The total weight of the glass tube including adsorbent and the needle was measured at regular intervals by an analytical balance (AR224CN, OHAUS). Then the absorbed \( \text{CO}_2 \) could be calculated through the weight increase of the glass tube. After that, dried \( \text{N}_2 \) was bubbled through the solution to regenerate the absorbent. The absorption of pure \( \text{N}_2 \) in [TEPA]Ac and [TEPA]Ac/PEG-200 mixtures at 353.15 K was also measured. The results showed that the content of \( \text{N}_2 \) absorbed by the [TEPA]Ac was less than 0.1%, which could be neglected during this study.

The viscosity of [TEPA]Ac/PEG-200 during the absorption of \( \text{CO}_2 \) was measured by a shear rate-controlled rheometer (Brookfield R/S plus) equipped with a shear vane (four blades with 20 mm in width and 40 mm in length).

2.4 Solubility of \( \text{CO}_2 \) in [TEPA]Ac/PEG-200 mixtures

\( \text{CO}_2 \) solubility measurement was performed on the basis of the isochoric saturation method [27]. Figure 2 shows the apparatus to measure \( \text{CO}_2 \) solubility. This device mainly consists of a \( \text{CO}_2 \) gas equilibrium cell (50 cm\(^3\)) with a magnetic stirrer, a gas reservoir (1000 cm\(^3\)), an oil bath and a pressure gauge (0-1.0 bar) with an accuracy of 0.0005 bar. The temperature of the oil bath was controlled by the thermo controller.
In a typical experiment, about 5g of [TEPA]Ac/PEG-200 was loaded into the equilibrium cell and degassed at 298.15 K under vacuum for at least 1 h. The mass of the absorbent was determined by the electronic balance. At a fixed oil-bath temperature, the valve of V₃ was closed, V₁, V₂ and V₄ were opened and the whole system was evacuated to pressure p₁. Then V₁ and V₄ were closed and V₃ was opened. The gas reservoir was loaded with CO₂ from the gas cylinder until the pressure reached a scheduled value (P₂), which was closed to atmospheric pressure. After that, V₂ and V₃ were closed and V₁ was opened. Then CO₂ was charged into the equilibrium cell and began being dissolved by [TEPA]Ac/PEG-200 while stirring. It was assumed that equilibrium was reached after the pressure of the system had been constant for 3 h. The final pressure was recorded as p₃. The equilibrium partial pressure of CO₂ was obtained as (p₃–p₁). Then V₁ was closed and the mass of cell was determined. The total CO₂ amount in the equilibrium cell was easily obtained by the masses of cell with and without absorbent.

Fig. 2 Experimental device for measurement of CO₂ solubility. ① Oil bath; ② CO₂ gas equilibrium cell; ③ CO₂ gas reservoir; ④ Cylinder filled with pure CO₂; V1-V4, Valves; (P) Pressure transmitter; (T) Thermo controller.
without the charge of CO₂. Since the experiment was conducted at sub-atmospheric pressure and above the room temperature, the mass of gaseous CO₂ in the equilibrium cell could be calculated based on the ideal gas law. Therefore, the content of CO₂ in the absorbent could be calculated by deducting the mass of gaseous CO₂ from the total CO₂ amount.

In this work, the solubility of CO₂ in the [TEPA]Ac/PEG-200 mixtures with the mass ratio of [TEPA]Ac to PEG-200 at 1:1, 1:2 and 1:3 were measured at four temperatures (353.15 K, 368.15 K, 383.15 K, and 395.15 K). The amount of CO₂ absorbed in the absorbent can be calculated by the following equation,

\[ n_{\text{CO}_2} = \frac{(m_2 - m_1)}{44} - \frac{(P_2 - P_1)}{RT} \left( V_{\text{cell}} - V_{\text{mixture}} \right) \]                     (1)

where \( V_{\text{cell}} \) is the volume of gas equilibrium cell; \( V_{\text{mixture}} \) represents the volume of the [TEPA]Ac/PEG-200 mixture. The \( m_2 \) and \( m_1 \) are the mass of the cell containing [TEPA]Ac/PEG-200 before and after loading CO₂ into the cell, respectively. Besides, 44 is the molecular mass of CO₂.

The volume of [TEPA]Ac/PEG-200 mixtures increased about 3% after saturated with CO₂. Therefore, the effect of expansion of [TEPA]Ac/PEG-200 mixtures on solubility calculation of CO₂ can be neglected.

3. Results and discussion

3.1 Absorption and desorption of CO₂

Based on the mechanism for the ILs with amine to capture CO₂ reported in some literatures [19, 28], it can be proposed that the process of CO₂ absorption and desorption in [TEPA]Ac should follow the mechanism as shown in Scheme 1.
Scheme 1: Mechanism on absorption and desorption of CO₂ by [TEPA]Ac

Figure 3 shows the results from experiments on absorption and desorption of CO₂ in/from [TEPA]Ac/PEG-200 mixtures with the mass ratio of 1:0, 1:1, 1:2, and 1:3. For the [TEPA]Ac/PEG-200 mixtures, the experiments were conducted at T = 353.15 K with CO₂ and N₂ of ambient pressure. For the pure [TEPA]Ac, the experiments were carried out at 383.15 K because the viscosity of [TEPA]Ac became very high (1550 mPa·s, Table 1) after absorbing CO₂ at T = 353.15 K. The content of PEG-200 has a strong effect on the CO₂ absorption rate (Fig. 3). The equilibrium absorption time was around 160 min for pure [TEPA]Ac. With the content of PEG-200 increased, the CO₂ absorption rate of [TEPA]Ac/PEG-200 mixtures increased dramatically even at a lower temperature (Figure 3). For example, the time required for CO₂ absorption up to saturation is about 85 min, 39 min, and 27 min at 353.15 K when the mass ratio of [TEPA]Ac to PEG-200 equals 1:1, 1:2, and 1:3, respectively.
**Fig. 3** Cycles of CO$_2$ absorption and desorption by [TEPA]Ac and [TEPA]Ac/PEG-200 mixtures: a) $W_{[TEPA]Ac}/W_{PEG-200} = 1 : 0$ at $T = 383.15$ K; b) $W_{[TEPA]Ac}/W_{PEG-200} = 1 : 1$ at $T = 353.15$ K; c) $W_{[TEPA]Ac}/W_{PEG-200} = 1 : 2$ at $T = 353.15$ K; d) $W_{[TEPA]Ac}/W_{PEG-200} = 1 : 3$ at $T = 353.15$ K.

As shown in Figure 3, the capacities of [TEPA]Ac/PEG-200 mixtures are similar and the mole ratio of CO$_2$ to [TEPA]Ac is about 1.24 at 353.15 K, which is higher than other IL-based absorbents that reported by other authors even at a higher temperature (Table 1). Besides, the effect of PEG-200 content on the capacity of CO$_2$ absorption by [TEPA]Ac was not significant, which indicates that the contribution of PEG-200 to the absorption of CO$_2$ is very limited. The reason is that the CO$_2$ could hardly be absorbed by PEG-200 at ambient pressure.
However, PEG-200 played the role as solvent for [TEPA]Ac and could increase the efficiency of CO\(_2\) absorption significantly. In the desorption process, the absorbed CO\(_2\) can be easily released by bubbling dried N\(_2\) through the solution. Besides, the results for ten cycles of CO\(_2\) absorption and desorption by [TEPA]Ac/PEG-200 mixture (W\(_{[\text{TEPA}]/\text{PEG-200}} = 1 : 3\)) are shown in Fig. 4. It can be seen that no observed loss of absorption capacity was found during the ten cycles, indicating that the absorbent can be completely regenerated.

Table 1. Comparisons of CO\(_2\) capacity and viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) with IL-based absorbents around the ambient pressure.

<table>
<thead>
<tr>
<th>Absorbents</th>
<th>Temperature, K</th>
<th>mol CO(_2)/mol IL</th>
<th>Viscosity, mPa·s</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before absorption</td>
<td>After absorption</td>
<td></td>
</tr>
<tr>
<td>[TEPA]Ac/PEG-200</td>
<td>353.15</td>
<td>1.24(^b)</td>
<td>30</td>
<td>78</td>
</tr>
<tr>
<td>[TEPA]Ac</td>
<td>353.15</td>
<td>1.24</td>
<td>130</td>
<td>1550</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{Ile}])</td>
<td>353.15</td>
<td>----</td>
<td>97</td>
<td>1300</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{Gly}])</td>
<td>353.15</td>
<td>----</td>
<td>95</td>
<td>650</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{Ile}])</td>
<td>298.15</td>
<td>0.97(^c)</td>
<td>430</td>
<td>100000</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{Ala}])</td>
<td>298.15</td>
<td>0.66(^c)</td>
<td>450</td>
<td>53000</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{Sar}])</td>
<td>298.15</td>
<td>0.91(^c)</td>
<td>440</td>
<td>83000</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{o-AA}])</td>
<td>303.15</td>
<td>0.60</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{o-AA}])</td>
<td>343.15</td>
<td>0.16</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>[P(_{66614})]([\text{p-AA}])</td>
<td>303.15</td>
<td>0.92</td>
<td>----</td>
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</tr>
<tr>
<td></td>
<td>Mole Ratio of CO\textsubscript{2} to [TEPA]Ac</td>
<td>Cycle</td>
<td></td>
<td></td>
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<tr>
<td>----------------</td>
<td>---------------------------------------------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P\textsubscript{66614}][ p-AA]</td>
<td>343.15 0.41</td>
<td>[31]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[DETA]-Cl/EG (R\textsuperscript{d} = 4.0)</td>
<td>303.15 0.90</td>
<td>[32]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[DETA]-Cl/EG (R\textsuperscript{d} = 4.0)</td>
<td>323.15 0.71</td>
<td>[32]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[emim][2-CNPy]r</td>
<td>295.15 0.80</td>
<td>[33]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[emim][4-Triaz]</td>
<td>295.15 0.72</td>
<td>[33]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[emim][3-Triaz]</td>
<td>295.15 0.53</td>
<td>[33]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* M stands for mass ratio of PEG-200 to [TEPA]Ac.

*b* mol CO\textsubscript{2}/mol [TEPA]Ac.

*c* Solubility of CO\textsubscript{2} was calculated by linear interpolation of the nearest experimental data points.

*d* R stands for mole ratio of EG to [DETA]-Cl.

---

**Fig. 4** Cycles of CO\textsubscript{2} absorption and desorption by [TEPA]Ac/PEG-200 mixture

\[ \frac{W_{[\text{TEPA} \text{Ac}]}}{W_{\text{PEG-200}}} = 1 : 3 \]

3.2 Viscosity of the hybrid absorbent during the CO\textsubscript{2} absorption

Although [TEPA]Ac/PEG-200 has excellent properties, such as good circulation performance and high CO\textsubscript{2} capacity at high temperatures, the viscosity of IL will increase
with absorbing CO$_2$ just as the other IL-based adsorbents [4, 30]. For example, the viscosity of [P$_{66614}$][Ala] increased from 450 mPa·s to 53000 mPa·s after saturated with CO$_2$ (Table 1), which has a serious effect on the application of it for the capture of CO$_2$. Viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) after the CO$_2$ absorption at 353.15 K was measured, and the result is shown in Figure 5. The viscosity of [TEPA]Ac/PEG-200 mixture increased during the CO$_2$ absorption. The reason for increasing viscosity of [TEPA]Ac/PEG-200 after absorbing CO$_2$ is the formation of a hydrogen bond network during the CO$_2$ absorption by [TEPA]Ac [34]. The viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) before and after the CO$_2$ absorption was compared with other IL-based absorbents reported in the literatures (Table 1). It can be seen from Table 1, the viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1:3) is just 78 mPa·s after saturation with CO$_2$, which is much lower than that of the other CO$_2$-saturated IL-based adsorbents.

![Viscosity of [TEPA]Ac/PEG-200](image)

**Fig. 5.** Viscosity of [TEPA]Ac/PEG-200 (mass ratio = 1 : 3) during the absorption of CO$_2$ at 353.15 K
3.3 Solubility of CO$_2$ in [TEPA]Ac/PEG-200 mixtures

The study of solubility of CO$_2$ at equilibrium condition is very important and valuable for both fundamental research and practical applications of the [TEPA]Ac/PEG-200 mixtures. The results of the CO$_2$ solubility in the [TEPA]Ac/PEG-200 mixtures with different mass ratio and at four temperatures (353.15 K, 368.15 K, 383.15 K, and 395.15 K) were shown in Table 2, where $x_1$ and $P$ represents the mole fraction of CO$_2$ in the absorbent and the equilibrium pressure, respectively.

**Table 2** Mole ratio of CO$_2$ to [TEPA]Ac ($M_{CO_2}/M_{[TEPA]Ac}$) at different temperatures and pressures.

<table>
<thead>
<tr>
<th>$W_{IL}/W_{PEG-200}$</th>
<th>$T$ / K</th>
<th>$P$ / bar</th>
<th>$x_1$ *</th>
<th>$M_{CO_2}/M_{[TEPA]Ac}$</th>
<th>$W_{IL}/W_{PEG-200}$</th>
<th>$T$ / K</th>
<th>$P$ / bar</th>
<th>$x_1$ *</th>
<th>$M_{CO_2}/M_{[TEPA]Ac}$</th>
<th>$W_{IL}/W_{PEG-200}$</th>
<th>$T$ / K</th>
<th>$P$ / bar</th>
<th>$x_1$ *</th>
<th>$M_{CO_2}/M_{[TEPA]Ac}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>353.15</td>
<td>0.0455</td>
<td>0.0373</td>
<td>0.0838</td>
<td>368.15</td>
<td>0.0585</td>
<td>0.0554</td>
<td>0.1243</td>
<td>0.0185</td>
<td>383.15</td>
<td>0.2205</td>
<td>0.2889</td>
<td>0.6485</td>
<td>0.2095</td>
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<tr>
<td></td>
<td>0.0195</td>
<td>0.0168</td>
<td>0.0585</td>
<td>0.2205</td>
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<td>0.0168</td>
<td>0.0585</td>
<td>0.2205</td>
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<td>0.0585</td>
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<td></td>
<td>0.0050</td>
<td>0.0087</td>
<td>0.0380</td>
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<tr>
<td>0.6165</td>
<td>0.3909</td>
<td>0.8775</td>
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* $x_1$, mole ratio of CO$_2$ to [TEPA]Ac/PEG-200 mixture

Figure 6 illustrates the isothermal solubility behavior of the [TEPA]Ac/PEG-200 mixtures at different temperatures. The solubility of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures increased significantly with the increase of pressure. The CO$_2$ solubility is more sensitive to pressure in the low-pressure range. Also, it was shown that at each pressure, the solubility of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures decreased with the increasing of temperature (Fig.
Fig. 6 Dependence of the solubility of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures on temperature and pressure: a) $W_{[TEPA]Ac} / W_{PEG-200} = 1 : 1$; b) $W_{[TEPA]Ac} / W_{PEG-200} = 1 : 2$; c) $W_{[TEPA]Ac} / W_{PEG-200} = 1 : 3$ (x$_1$, mole ratio of CO$_2$ to [TEPA]Ac/PEG-200 mixture)

At the same temperature and pressure, the solubility of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures decreased with the increase of the PEG-200 content. The reason is that the PEG-200 could hardly absorb CO$_2$ at each temperature and pressure which has been discussed above. Distribution of the molar ratio of CO$_2$ to [TEPA]Ac ($M_{CO_2}/M_{[TEPA]Ac}$) in the experiment at different [TEPA]Ac to PEG-200 mass ratios was shown in Figure 7 in order to describe
clearly the role of [TEPA]Ac and PEG-200 for the CO$_2$ absorption. The effect of the mass ratio of [TEPA]Ac to PEG-200 on the M$_{CO_2}$/M$_{[TEPA]Ac}$ is very limited. Almost all amount of CO$_2$ was absorbed by [TEPA]Ac due to the strong interaction between the basic group of [TEPA]Ac and CO$_2$.

Fig. 7 The effect of temperature and pressure on the molar ratio of CO$_2$ to [TEPA]Ac (M$_{CO_2}$/M$_{[TEPA]Ac}$): a) T = 353.15 K; b) T = 368.15 K; c) T = 383.15 K; d) T = 398.15 K.

3.4 Enthalpy and entropy of solution

The strength of interaction between CO$_2$ and absorbent can be reflected by enthalpy ($\Delta H_{sol}$), and the order degree changing of solution during the capture of CO$_2$ can be reflected
by entropy ($\Delta S_{sol}$), i.e. the $\Delta H_{sol}$ and $\Delta S_{sol}$ are important thermodynamic parameters for the investigated system. $\Delta H_{sol}$ and $\Delta S_{sol}$ can be calculated through the following equations [35]:

$$\frac{\Delta H_{sol}}{R} = \left( \frac{\partial \ln P}{\partial (1/T)} \right)_{x_1}$$

$$\frac{\Delta S_{sol}}{R} = - \left( \frac{\partial \ln P}{\partial T} \right)_{x_1}$$

where $x_1$ is the mole fraction of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures, $R$ is the molar gas constant. In the system investigated in this work, $\ln P$ had a linear relationship with $1/T$ and $\ln T$ at fixed $x_1$. For example, the dependence of $\ln P_1$ on $1/T$ at $x_1 = 0.055$ and $W_{IL}/W_{PEG-200} = 1:1$ was shown in Figure 8. The values of $\Delta H_{sol}$ and $\Delta S_{sol}$ at four fixed values of $x_1$ for each [TEPA]Ac/PEG-200 mixture were calculated and listed in Table 3.

**Fig. 8** Relationship between $\ln P$ and $1/T$ or $\ln T$ at $x_1 = 0.055$ for the [TEPA]Ac/PEG-200 mixture with the mass ratio of 1:1

**Table 3** Enthalpy (kJ/mol) and entropy (J/K mol$^{-1}$) of solution of CO$_2$ in the [TEPA]Ac/PEG-200 mixtures ($T = 353.15$-$395.15$K)

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<tr>
<th>$W_{[\text{TEPA}]Ac}/W_{\text{PEG-200}}$</th>
<th>$1:1$</th>
<th>$1:2$</th>
<th>$1:3$</th>
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<tbody>
<tr>
<td>$W_{[\text{TEPA}]Ac}/W_{\text{PEG-200}}=1:1$</td>
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<tr>
<td>$W_{[\text{TEPA}]Ac}/W_{\text{PEG-200}}=1:2$</td>
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<td>$W_{[\text{TEPA}]Ac}/W_{\text{PEG-200}}=1:3$</td>
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</table>
Under all conditions, the $\Delta H_{\text{sol}}$ of absorbents has negative values indicating that a large amount of heat is released during the absorption process. This feature should be taken into consideration during the process of practical application. Also, the large negative values of $\Delta H_{\text{sol}}$ indicate that the interaction between the [TEPA]Ac/PEG-200 mixtures and CO$_2$ is quite strong. The $\Delta S_{\text{sol}}$ can reflect structure change of the absorbent before and after the CO$_2$ absorption. Thus, the negative values of $\Delta S_{\text{sol}}$ demonstrate that the structure of the [TEPA]Ac/PEG-200 mixtures has higher ordering degree after the absorption of CO$_2$.

4. Conclusions

The [TEPA]Ac/PEG-200 mixture is a new type of IL-based absorbent for CO$_2$ capture. It has excellent properties, such as good circulation performance and high CO$_2$ capacity at high temperatures. The main conclusions can be summarized as follow:

The [TEPA]Ac/PEG-200 mixtures have high CO$_2$ absorption capacity and the mole ratio of CO$_2$ to [TEPA]Ac can reach 1.24 at 353.15 K under the ambient pressure (1.01 bar). Moreover, the absorbents can absorb CO$_2$ effectively at a higher temperature indicating that
they have potential application to capture CO₂ from flue gas in the industry.

The [TEPA]Ac/PEG-200 mixtures with CO₂ absorbed can be easily regenerated by bubbling N₂ through the absorbents. No observed loss of absorption capacity was found during ten absorption and desorption circulations, indicating that the absorbent can be completely regenerated.

The addition of PEG-200 increased significantly the CO₂ absorption efficiency of the absorbent.

The solubility of CO₂ in the [TEPA]Ac/PEG-200 mixtures decreased with increasing temperature or decreasing CO₂ partial pressure.

The CO₂ absorption in the [TEPA]Ac/PEG-200 mixtures is an exothermic process and the ordering degree of the absorbent structure increases during the CO₂ absorption.

**Acknowledgements**

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**References**


[31] Xiao Y. Luo, Fang Ding, Wen J. Lin, Yu Q. Qi, Hao R. Li, and Cong M. Wang, Efficient and Energy-Saving CO₂ Capture through the Entropic Effect Induced by the Intermolecular Hydrogen Bonding


