Performance and reaction kinetics of CO₂ absorption into AMP solution with [Hmim][Gly] activator

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Absorption and regeneration of a new aqueous blend of 1-hexyl-3-methylimidazolium glycinate ([Hmim][Gly]) and 2-amino-2-methyl-1-propanol (AMP) were investigated. The physicochemical properties of [Hmim][Gly]-AMP mixed solution with varying molar ratios were obtained at different temperature, and the results demonstrated that the mixed solution had a low viscosity with a high solubility of CO₂. It was found that the reactivity of AMP was significantly enhanced with the addition of [Hmim][Gly], and the absorption of CO₂ into the mixed solution was independent of temperature within a range of 298–323 K. The optimal regeneration temperature and time were 333 K and 60 min, respectively. The mixed solution could be regenerated efficiently after three cycles. Furthermore, the study of 13C NMR spectrum indicated that the reaction between CO₂ and the [Hmim][Gly]-AMP solution was zwitterionic mechanism. Based on zwitterionic mechanism and two-film model, the kinetics of CO₂ absorption into the mixed solution was investigated in the temperature range of 298–323 K by employing a double stirred-cell absorber. The kinetics region was considered to be a fast pseudo-first order, and the second order reaction rate constant was calculated as follows: $k_s[Hmim][Gly]$-AMP = $1.57 \times 10^{8}$ (mol·L$^{-1}$·s$^{-1}$·kPa$^{-1}$).

1. Introduction

Large emissions of CO₂ have caused negative effect on atmospheric environment. Many countries have done jointing effort to reduce CO₂ emissions (Miller et al., 2010). Chemical absorption using alkanolamine aqueous solution is generally considered as a reliable technology for CO₂ capture. Monoethanolamine (MEA), a primary amine, is widely used for post-combustion capture from power plant for its rapid reaction rate with CO₂ and low molecular weight (Tan et al., 2011). However, the regeneration of MEA requires high energy due to the high absorption heat. Some studies also showed that the degradation rate of MEA increased as temperature rose (Zheng et al., 2012). Therefore, there is a highly requirement to develop new chemical absorbents.

Ionic liquids (ILs), generally consist of large organic bulky asymmetric cation (e.g. quaternary ammonium, imidazolium, pyridiniumand phosphonium ions) and small symmetrical shaped anion. They are regarded as promising green absorbents for CO₂ absorption, due to many fascinating properties, such as negligible volatility, non-flammability, high chemical and thermal stability, excellent solubility for CO₂, easy to be recycled and fine structure and property tunability (Wu et al., 2011; Zhang et al., 2006, 2013). Compared with other ILs, amino acid ionic liquids (AAILs) are more biodegradable and biocompatible, even when they contain imidazolium cation. Meanwhile, amino acids (AAs) are easy to be obtained in large quantities at low cost (Sharma et al., 2012). In 2005, Ohno’s group (2005) prepared AAILs ([emim][AA]) from 20 natural AAs. Lu et al. (2011) synthesized three imidazolium AAILs absorbents ([bmim][Gly], [bmim][Ala], [bmim][Lys]) for CO₂ absorption. Their results revealed that the absorption loading and the absorption rate of these AAILs were much larger than that of the original AAs solution. In appropriate conditions, the regeneration efficiency of these imidazolium AAILs almost reached 100% (Zhao et al., 2011).

Since pure AAILs have a higher viscosity than the ordinary ILs and are not conducive to the actual absorption, the industrial application of them as CO₂ absorbent is still unfeasible. Fortunately, most of the AAILs are soluble in water, and the viscosity reduces obviously in aqueous solution. Zhang et al. (2010) found that CO₂ absorption into a new aqueous solution of tetramethylammonium glycinate [N$_{1111}$][Gly] exhibited a high absorption capacity. The CO₂ loading of the saturated absorption solution was increased from 0.169 to 0.601 mol CO₂/mol IL as the mass fraction of [N$_{1111}$][Gly]...
MDEA, the sterically hindered amine AMP has the same high equilibrium capacity for CO2, but a higher reaction rate constant (Saha et al., 1995) and a lower regeneration energy cost (Mandal et al., 2001, 2003). Therefore, in our previous work (Zhou et al., 2012), [N1111][Gly] was mixed with AMP aqueous solution to form a new solvent for CO2 absorption. The results indicated that [N1111][Gly] promoted the absorption of CO2 in 0.95 M (mol L−1) AMP aqueous solution. In our previous work, the second-order reaction rate of CO2 absorption into [Hmim][Gly] was found to be $k_2 = 3.04 \times 10^{7}$ exp$(-3050/T)$ (Guo et al., 2013), while that of [N1111][Gly] was found to be $k_2 = 4.6930 \times 10^{6}$ exp$(-1.856/T)$ (Jing et al., 2012). Thus, the absorption rate of CO2 into [Hmim][Gly] solution was higher than that of the [N1111][Gly] solution. Hence the mixed solution of [Hmim][Gly]-AMP seems to be worth exploring for CO2 capture.

In this work, a mixed aqueous solution consisted of [Hmim][Gly] and AMP was proposed for CO2 absorption. The performance of CO2 absorption and regeneration with the new absorbent were investigated at different mole ratio of [Hmim][Gly]-AMP, reaction temperature, regeneration temperature and regeneration time. The mechanism of CO2 capture into this new absorbent was proposed based on 13C NMR spectra analysis, and the kinetic rate parameters were determined by a double stirred-cell absorber based on two-film model.

2. Experimental and methods

2.1. Chemicals

[Hmim][Gly] (97%) was obtained from Shanghai Cheng Jie Chemical Co. LTD. China. AMP was purchased from J&K Scientific Ltd. Aqueous solution was prepared with distilled water. The gases were pure CO2 (>99.999% purity) and N2 (>99.999% purity) obtained commercially and used as received.

2.2. Absorption and regeneration methods

A double stirred-cell absorber with a smooth gas–liquid interface was used as the absorption instrument, which was reported in detail in our previous work (Jing et al., 2012). The experiments were conducted with simulated flue gas, which mixed with 85% N2 and 15% CO2 of volume ratio. The gas flow rate was adjusted to 120 mL min−1 by mass flow controller. The stirring speed for gas phase was 250 rpm and for liquid phase was 130 rpm. The total concentration of the absorbent was 1.0 M. The absorption temperature was from 298 K to 323 K. The kinetics region was determined according to the judge method suggested by Levenspiel and Godfrey (1974).

The absorption rate of CO2 can be calculated as follows:

$$N = \frac{P \times (V_{out} - V_{in})}{ART}$$

where A, P, R, T are gas–liquid interfacial area (m²), pressure (Pa), ideal gas law constant (kmol m$^{-3}$ s$^{-1}$), temperature (K), respectively. $V_{in}$, $V_{out}$ are volumetric flow rate of inlet, outlet CO2 (m³ s$^{-1}$), respectively.

The CO2 saturated loading in the [Hmim][Gly]-AMP mixed solution was measured by a bubbling absorber, which had used in our previous work (Guo et al., 2013). The absorption took place in a flask with 100 mL mixed solution. The simulated flue gas flowed through a soap bubble meter to measure the flow rate after heated to the desired temperature of 303 K by a heating oven. The volumetric flow rate of the exit gas was also determined by another soap bubble meter. The CO2 loading was obtained by calculating the integral characteristic value of absorption rate to time, using Origin 8.0. Regeneration experiments were investigated under 0.5 kPa vacuum for a certain time by using a rotary evaporator to obtain
the optimal regeneration temperature and regeneration time. After regeneration, the repeated absorption was performed under the same conditions with the barren solution. The regeneration efficiency can be calculated as:

$$\eta = \frac{L_2}{L_1}$$  \hspace{1cm} (2)

$\eta$ is the regeneration efficiency (%); $L_1$ and $L_2$ are the saturated absorption loading (mol CO₂/mol absorbent) for the first cycle of the fresh solution and $n$ cycle of the regenerated barren solution, respectively.

2.3. ¹³C NMR analysis

To gain a further insight into the absorption/desorption mechanism, 0.5 mL of the absorption samples of solvents before and after CO₂ absorption were characterized by ¹³C NMR (Bruker AVIII 500 MHz), using an internal standard of 0.1 mL D₂O for the deuterium lock.

2.4. Physicochemical data measurement and calculation

2.4.1. Density, viscosity and pH

The density, viscosity and pH of the [Hmim][Gly]-AMP solution were measured by acidity meter (pH5-25), Anton Paar Density meter (DMA 4500) and digit display viscometer (NDJ-5S), respectively.

2.4.2. Solubility of CO₂ in the mixed solution of [Hmim][Gly]-AMP

The solubility of CO₂ in the pure [Hmim][Gly] was calculated by regular solution theory (Scovazzo et al., 2004), which was reported in our previous works (Guo et al., 2013). Moreover, the Henry's constant ($H$) and the solubility parameter ($\delta_1$) of CO₂ in [Hmim][Gly] could be estimated. The Henry's coefficient (H, mol Pa⁻¹ m⁻³) of CO₂ in the pure AMP was determined by "N₂O analogy" method (Versteeg and Van Swaaij, 1988), the expression as follows:

$$H_{2,4} = H_{N_2,0.4} \times \frac{H_{2,3}}{H_{N_2,0.3}}$$ \hspace{1cm} (3)

Subscript 1, 2, 3, 4 stand for IL, CO₂, water and AMP, respectively. $H_{N_2,0.4}$, $H_{N_2,0.3}$, $H_{2,3}$ are determined by the expressions:

$$H_{N_2,0.4} = 8.648 \times 10^4 \exp \left(- \frac{1205.2}{T} \right)$$ \hspace{1cm} (4)

$$H_{N_2,0.3} = 8.55 \times 10^4 \exp \left(- \frac{2284}{T} \right)$$ \hspace{1cm} (5)

$$H_{2,3} = 2.82 \times 10^6 \exp \left(- \frac{2044}{T} \right)$$ \hspace{1cm} (6)

The data should be transformed between Henry's coefficient and Henry's constant (Pa). At the beginning of CO₂ absorption, the following expression can be used:

$$H \approx 10^6 \cdot \frac{\rho}{M \cdot H^*}$$ \hspace{1cm} (7)

$\rho$ (g cm⁻³), $M$ (g mol⁻¹) denote the average density and average molecular weight of the absorbent.

O'Connell and Prausnitz (1964) deduced the thermodynamic of $H$ in mixed solvents based on regular solution theory. They considered $H^*$ in the mixed solvent as a function of the nonideality of the solute-free solvent mixture as described by Eq. (8).

$$\ln H_{2,m}^* = \sum_{j=1}^{n} x_j \ln H_{2,j}^* - \sum_{j=1}^{n-1} \sum_{k>j}^{n} \alpha_{jk} x_j x_k$$ \hspace{1cm} (8)

$x$ stands for the mole fraction, subscript m for the mixed solution of [Hmim][Gly]-AMP, and $j, k$ for the different components in the mixed solution. $\alpha$ describes the interaction coefficient between the two different solvents, and $\alpha_{jk}$ can be estimated by a simplified form of Hildebrand's equation (O'Connell and Prausnitz, 1964):

$$\alpha_{jk} \approx \frac{(\delta_j + \delta_k)^2 (V_j + V_k)}{2RT}$$ \hspace{1cm} (9)

By definition, the solubility parameter of AMP can be calculated by Eq. (10):

$$\delta_4 = \left(\frac{\Delta E}{V_4} \right)^{1/2} = \left(\frac{\Delta H - RT}{V_4} \right)^{1/2}$$ \hspace{1cm} (10)

$\Delta H$ stands for the vaporization enthalpy of AMP, and the value is 47.05 kJ mol⁻¹ at the boiling point of 400 K obtained from Scifinder database. $\Delta E$ stands for cohesion energy density. $V$ represents the molar volume (cm³ mol⁻¹). The density of AMP was obtained according to the following equation (Xu et al., 1991).

$$\rho_4 = 0.9507 \times 10^3 - 0.7102 \times (T - 273) - 7.1246 \times 10^{-4} \times (T - 273)^2$$ \hspace{1cm} (11)

The solubility decreased with increasing solution temperature ($T_s$) in the condition of $T_s - T_b < 150$ K, while $T_b$ is below boiling point ($T_b$), and the expression can be shown as follows:

$$\frac{\delta_b}{\delta_a} = \left(\frac{\rho_b}{\rho_a} \right)^{1.13}$$ \hspace{1cm} (12)

Therefore, the solubility of CO₂ in the mixed solution can be obtained from Eq. (3) to Eq. (12).

2.4.3. Diffusivity of CO₂ in the mixed solution of [Hmim][Gly]-AMP

The diffusivity of CO₂ in the [Hmim][Gly]-AMP solution can be calculated by the model of Danckwerts (1970), shown in Eq. (13).

$$D_{2,m \mu m} T = D_{2,m} \mu T = \text{const}$$ \hspace{1cm} (13)

Here, $D$ denotes the diffusion coefficient (m² s⁻¹), $\mu$ denotes viscosity (mPa s). The value of $\mu$ was reported in the literature (Korson et al., 1969). $D_{2,3}$ can be calculated by the following equation (Korson et al., 1969).

$$\log D_{2,3} = -8.1764 + 712.5 \frac{T}{T} - 2.591 \times 10^{5} \frac{T}{T^2}$$ \hspace{1cm} (14)

3. Results and discussion

3.1. The physicochemical properties of [Hmim][Gly]-AMP solution

Table 1 shows the physicochemical value of [Hmim][Gly]-AMP solution with various components (0:1, 1:9, 2:8, 3:7) at different temperature (298–303 K). The pH, density and viscosity of the mixed solution were all increased with increasing [Hmim][Gly] concentration, but decreased as temperature increased. For each composition, there was a good linear relationship between ln($\rho_m$) and temperature ($T$), ln($\mu$) and ($T$ − 273.15) in a temperature range of 298–323 K. A higher IL concentration means a higher density and
viscosity, which will decrease the solubility and diffusivity of CO₂ in the mixed solution. The solubility of CO₂ decreased and the diffusivity of CO₂ increased with increasing temperature. The results were consistent with the predictions of Arrhenius equation and the thermodynamic diffusion mechanism.

3.2. Absorption of CO₂ into [Hmim][Gly]-AMP aqueous solution

3.2.1. Effect of [Hmim][Gly]-AMP mole ratio on CO₂ absorption rate

[Hmim][Gly] was added into AMP aqueous solution as an activator to form mixed absorbent. CO₂ absorption into the mixed solution was investigated at three different molar ratios of [Hmim][Gly]-AMP (1:9, 2:8, 3:7) with a total concentration of 1.0 M at 303 K and atmospheric pressure. As shown in Fig. 1, the absorption rate and absorption amount of CO₂ into the mixed solution were increased with increasing [Hmim][Gly] concentration at the same absorption time. Although the viscosity of [Hmim][Gly]-AMP aqueous solution also increased as [Hmim][Gly] concentration rose, the increasing rate was rather small (see in Table 1). The results indicated that the promotive effect of [Hmim][Gly] concentration on CO₂ absorption was more significant than that on the viscosity. With all the concentrations investigated, the absorption rates were fast at the first 15 min and decreased quickly due to the chemical absorption. Further increasing the reaction time resulted in a decrease of the absorption rate due to the saturation of the [Hmim][Gly]-AMP absorbt. The detailed discussion of the reaction would be shown in Section 4.

3.2.2. Effect of temperature on the absorption

In order to study the effect of temperature on CO₂ absorption, [Hmim][Gly]-AMP solution with a molar ratio of 3:7 was selected for CO₂ capture in a temperature range of 298–323 K. As shown in Fig. 2, temperature had little influence on the absorption rate in the investigated range. This result was similar to that of the system consisted of 15% [N₁₁₁₁][Gly] + 15% MDEA for CO₂ absorption (Zhang et al. 2010). Our previous research found that temperature (298–323 K) could slightly affect the absorption of CO₂ in 1.0 M [Hmim][Gly] solution (Guo et al. 2013). Weng et al. (2011) had revealed that temperature (298–323 K) had little influence on the absorption of CO₂ in aqueous solutions of AMP or AMP + SG (sodium glycinate).

3.2.3. Interaction effect of [Hmim][Gly] and AMP in the mixed solution

As shown in Fig. 3, CO₂ absorption into [Hmim][Gly]-AMP aqueous solution was compared with that into single AMP solution and [Hmim][Gly] solution, respectively. The absorption rate of 0.3 M [Hmim][Gly] was higher than that of 0.7 M AMP at the first 30 min. As increasing the reaction time, the absorption rate of [Hmim][Gly] was finally lower than that of 0.7 M AMP. However, the absorption

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**Table 1**
The physicochemical properties of [Hmim][Gly]-AMP solution.

<table>
<thead>
<tr>
<th>(n_1:n_2)</th>
<th>T (K)</th>
<th>pH</th>
<th>(\rho_m ) (g cm(^{-3}))</th>
<th>(\rho_m ) (mPa s)</th>
<th>(\ln \rho_m = a(T - 273.15) + b)</th>
<th>(\ln \mu_m = aT + b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>298</td>
<td>12.11 ± 0.01</td>
<td>0.99645 ± 1.73E−5</td>
<td>1.25 ± 0.00</td>
<td>(a = 0.0004b = 0.0165r^2 = 0.9972)</td>
<td>(a = -0.0236 b = 7.35 r^2 = 0.9989)</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>11.95 ± 0.01</td>
<td>0.99521 ± 5.77E−6</td>
<td>1.19 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>11.76 ± 0.02</td>
<td>0.99137 ± 3.06E−5</td>
<td>0.87 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>11.57 ± 0.04</td>
<td>0.98685 ± 8.89E−5</td>
<td>0.70 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:9</td>
<td>298</td>
<td>11.42 ± 0.03</td>
<td>0.99968 ± 6.10E−4</td>
<td>1.34 ± 0.00</td>
<td>(a = 0.0004b = 0.0317r^2 = 0.9965)</td>
<td>(a = -0.0236 b = 7.3398r^2 = 0.9929)</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>11.28 ± 0.01</td>
<td>0.99833 ± 2.65E−5</td>
<td>1.15 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>11.08 ± 0.03</td>
<td>0.9944 ± 5.77E−6</td>
<td>0.90 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>10.88 ± 0.02</td>
<td>0.98992 ± 2.08E−5</td>
<td>0.74 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:8</td>
<td>298</td>
<td>11.45 ± 0.03</td>
<td>1.00283 ± 1.00E−5</td>
<td>1.36 ± 0.00</td>
<td>(a = 0.0004b = 0.0099r^2 = 0.9940)</td>
<td>(a = -0.0236 b = 7.318r^2 = 0.9929)</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>11.3 ± 0.01</td>
<td>1.00109 ± 5.77E−6</td>
<td>1.18 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>11.12 ± 0.03</td>
<td>0.99704 ± 1.00E−5</td>
<td>0.93 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>10.97 ± 0.04</td>
<td>0.99228 ± 1.13E−5</td>
<td>0.75 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3:7</td>
<td>298</td>
<td>11.45 ± 0.02</td>
<td>1.00545 ± 1.15E−5</td>
<td>1.39 ± 0.00</td>
<td>(a = 0.0004b = 0.0066r^2 = 0.9917)</td>
<td>(a = -0.0235 b = 7.2163r^2 = 0.9988)</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>11.27 ± 0.03</td>
<td>1.00358 ± 5.77E−6</td>
<td>1.24 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>11.11 ± 0.03</td>
<td>0.9994 ± 1.15E−5</td>
<td>0.96 ± 0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>10.91 ± 0.02</td>
<td>0.99457 ± 1.15E−5</td>
<td>0.77 ± 0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( n_1, n_2 \) stand for [Hmim][Gly] and AMP, respectively.
rate of 0.3 M [Hmim][Gly] or 0.7 M AMP was lower than that of their mixture. On the other hand, the absorption amount of 0.3 M [Hmim][Gly] + 0.7 M AMP, 0.3 M [Hmim][Gly], 0.7 M AMP solution were 0.04886, 0.0355, 0.0247 mol, respectively. The absorption amount of the mixed solution was less than that of the sum of each single solution. It could be seen that there was a weak negative interaction of [Hmim][Gly] and AMP on CO2 absorption in the mixed system.

3.3. Regeneration of [Hmim][Gly]-AMP saturated aqueous solution

Besides absorption characteristics, regeneration performance is also an important criterion for absorbent selection, especially in regards to the energy penalty in the regenerator. Hence, 0.3 M [Hmim][Gly] + 0.7 M AMP was chosen to study the effect of regeneration cycle, regeneration temperature (298–323 K) and regeneration time on CO2 regeneration.

3.3.1. Effect of regeneration temperature on regeneration efficiency

The mixed absorbent of 0.3 M [Hmim][Gly] + 0.7 M AMP was regenerated at temperature of 323–338 K. CO2 absorption loading of the mixed solution after regenerating at different temperature was compared with that of the fresh solution, and the results were shown in Fig. 4. The absorption rates of CO2 in all the solutions were rather fast in the first 90 min, and then decreased with increasing reaction time until the aqueous solution was saturated. The results showed that the mixed solution could be well regenerated by thermal method. On the other hand, CO2 loading increased with the increase of the regeneration temperature. However, it was of interest to note that there was only 7.20% increase in the regeneration efficiency from 333 to 338 K. For energy-saving, the appropriate regeneration temperature was 333 K.

3.3.2. Effect of regeneration time on regeneration efficiency

To explore the optimal regeneration time, the regeneration experiments were performed at four different regeneration time. As shown in Fig. 5, the CO2 saturated loading of the second absorption were 0.390, 0.463, 0.473, and 0.481 mol CO2/mol absorbent, while the regeneration time were 30, 60, 90 and 120 min, respectively. The CO2 saturated loading rose very slightly over 60 min. Thus, the optimal regeneration time was 60 min, and the corresponding regeneration efficiency was 94.68%.

3.3.3. Effect of absorption/regeneration cycles on regeneration efficiency

The mixed solution of [Hmim][Gly]-AMP was regenerated for three cycles at 333 K and 60 min. As illustrated in Fig. 6, the regeneration efficiency in turn was 96.73%, 95.30% and 94.07% for the first, the second and the third cycle regeneration, respectively.

![Fig. 3. CO2 absorption into [Hmim][Gly]-AMP solutions at 303K.](image)

![Fig. 4. CO2 loading of 0.3 M [Hmim][Gly] + 0.7 M AMP under different regeneration temperature.](image)

![Fig. 5. CO2 loading of 0.3 M [Hmim][Gly] + 0.7 M AMP under different regeneration time.](image)

![Fig. 6. Consecutive absorption and desorption of CO2 in recycled [Hmim][Gly]-AMP solution against time.](image)
regeneration efficiency of the solution after different regeneration cycles changed slightly, which revealed that the aqueous blend of [Hmim][Gly]-AMP was well recycled with a rapid absorption rate by thermal regeneration. There were two possible reasons for the slightly decrease in regeneration efficiency: the reaction of [Hmim][Gly] with CO₂ produced a number of heat-stable salts, which were unregenerate under the regeneration conditions (Winyu et al., 2006); the volatilization and degradation of AMP in the thermal regeneration process (Zheng et al., 2012).

4. Absorption mechanism

To gain a further insight into the absorption mechanism, the 13C NMR spectrum of CO₂-treated solution was compared with the initial ones in Fig. 7. The molecular structure and the types of carbon nuclei in the mixed solution visualized with the 13C NMR technique could be seen in Fig. 8. In the 13C NMR spectra (Fig. 7(b)), after capturing CO₂, a new peak observed at 160 ppm was attributed to HCO₃⁻ or CO₃²⁻. Therefore, the reaction mechanism between CO₂ and AMP (RNH₂) (where R' = C(CH₃)₂CH₂OH) is different from that of unhindered amines as shown in the following equations:

$$2R'NH_2 + CO_2 \rightarrow R'NHCOO^- + RNH_3^+ \quad (15)$$

$$R'NHCOO^- + H_2O \rightarrow R'NH_2 + HCO_3^- \quad (16)$$

Overall reaction:

$$R'NH_2 + CO_2 + H_2O \rightarrow R'NH_3^+ + HCO_3^- \quad (17)$$

The carbamate of AMP is easily hydrolyzed into AMP and bicarbonate (Sartori and Savage, 1983). As shown in Fig. 7(b), the 13C NMR spectrum of CO₂-saturated AMP solution did not contain a new resonance that corresponding to the formation of a
carbamate carbonyl carbon. This result indicated that AMP-carbamate had been fully hydrolyzed.

It was expected that CO2 reacted with a solution of AAILs through a zwitterionic mechanism similar to amines (Caplow, 1968; Danckwerts, 1979; Kumar et al., 2003), because of the similar functional groups. According to the zwitterionic mechanism and the 13C NMR spectrum (Fig. 7(c) and (d)), CO2 reacted with [Hmin][Gly] via the formation of a zwitterion, subsequently deprotonated by a base present in the solution ([Hmin]+ was represented as R+ in the following):

\[
\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{CO}_2 \rightleftharpoons \text{K}_2\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} \text{R}^+ (18)
\]

\[
-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{B}^+ \rightleftharpoons \text{B}^-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{H}^+ (19)
\]

\[
-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{B}^-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{H}_2\text{O}^- (20)
\]

where \(K_2\) and \(k_2\) are the equilibrium constant and the rate constant of the second order reaction. \(B^+\) is a base, which could be amine, \(\text{OH}^-\), or \(\text{H}_2\text{O}^-\). Different from the AMP-carbamate, as shown in Fig. 7(d), the 13C NMR spectrum contained a new resonance that corresponding to the formation of a carbamate carbonyl carbon. It showed that [Hmin][Gly]-carbamate did not thoroughly hydrolyzed.

In the [Hmin][Gly]-AMP solution, [Hmin][Gly] could react quickly with CO2 to form zwitterions, which would transfer protons to AMP, therefore, the absorption rate of CO2 increased greatly compared with the AMP aqueous solution. During CO2 absorption, \(\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} \text{R}^+\) was expected to be eliminated by plenty of AMP. The interaction between the protonated and the unprotonated amines, as shown in Eq. (24), involved only a proton transfer and was considered to be instantaneous and at equilibrium. According to the 13C NMR analysis (Fig. 7(f)), the forms of CO2 in an aqueous amine solution consisted of carbamate, biconate and carboxylic acid, thus the equilibrium reactions in the liquid phase were suggested as follows:

\[
-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{B}^-\text{OCO}^+\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{H}_2\text{O}^- (21)
\]

\[
\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{H}^+ + \text{O}^-\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{H}_2\text{O}^- (22)
\]

\[
\text{R}^-\text{NH}_2 + \text{H}^+ + \text{RH}_3^- (23)
\]

\[
\text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{R}^-\text{NH}_2 + \text{H}_2\text{N-CH}_2\text{-COO}^\text{-} + \text{R}^-\text{NH}_2 (24)
\]

\[
\text{CO}_2 + \text{H}_2\text{O}^+ + \text{H}_2\text{O}^- (25)
\]

\[
\text{H}_2\text{O}^- + \text{CO}_2 (26)
\]

\[
\text{H}_2\text{O}^+ + \text{OH}^- (27)
\]

5. Absorption kinetics

The kinetics region of CO2 absorption into the mixed absorbent of 0.3 M [Hmin][Gly] + 0.7 M AMP was carried out in different liquid-phase volumes and mass transfer coefficient at 303 K. As shown in Table 2, the change of the volume of liquid-phase on CO2 absorption rate had little effect and could be neglected. As was mentioned in Sections 3.2.1 and 3.2.3, the CO2 absorption rate increased with the increase of the absorbent concentration within our investigation conditions. According to the judgment suggested by Levenspiel and Godfrey, the kinetics region of CO2 absorption into the mixed solution was considered to be a fast pseudo-first order (Levenspiel and Godfrey, 1974).

The reaction kinetics could be determined by the two-film model which was detailed in our previous works (Jing et al., 2012). The gas-phase and liquid-phase mass transfers in the gas–liquid interface can be considered as follows:

\[
N = k_c (P_2 - P_{2,i}) (28)
\]

\[
N = E_{KL} C_{2,i} (C_{2,i} - C_2) (29)
\]

Here, \(k_c\) and \(k_l\) denote the gas-phase and liquid-phase mass transfer coefficients, obtained from the literature (Mandal et al., 2001), respectively. At the beginning, the concentration of CO2 in the bulk solution can be ignored \((C_2 = 0)\) relative to the ILs concentration. The \(C_1\) can be calculated by Eq. (30), on the basis of the phase balance in the gas–liquid interface:

\[
C_{2,i} = H_2P_{2,i} (30)
\]

Throughout the experiments, the kinetic parameters were calculated based on the initial CO2 absorption rates. As a result, the enhancement factor \((E)\) for CO2 absorption can be obtained from Eq. (31) by combining with Eqs. (28)–(30).

\[
E = \frac{N}{H_2k_c (P_2 - N/k_c)} (31)
\]

For the fast pseudo-first order reaction regime, the absorption rate was also given by Eq. (32). Details of the theory were introduced by Danckwerts (1970).

\[
N = C_{2,i} \sqrt{k_2D_2C_1} (32)
\]

According to Eqs. (28)–(32), the enhancement factor \((E)\) and the second-order forward rate constant \((k_2)\) can be determined.

The kinetic parameters for CO2 absorption are listed in Tables 3 and 4. The data summarized that \(E\) increased as the concentration of [Hmin][Gly] increased. Linear regression analysis of the values of the second-order reaction rate constant at various temperatures is shown in Fig. 9. The Arrhenius equation led the following expression:

\[
k_2[Hmin][Gly] \cdot \text{AMP} = 1.57 \times 10^{7} \exp \left( \frac{-3088.92}{T} \right) (33)
\]
Table 3  
The kinetic data for CO2 absorption in [Hmim][Gly]-AMP solution of 1 M total amine concentration with varying mole ratio at 303 K.  

<table>
<thead>
<tr>
<th>n1/n4</th>
<th>N0 × 103 (mol m⁻² s⁻¹)</th>
<th>E</th>
<th>k2 (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>1.74 ± 0.04</td>
<td>40.90 ± 2.93</td>
<td>496.12 ± 69.50</td>
</tr>
<tr>
<td>1:9</td>
<td>1.76 ± 0.00</td>
<td>43.65 ± 0.28</td>
<td>587.76 ± 8.29</td>
</tr>
<tr>
<td>2:8</td>
<td>1.90 ± 0.03</td>
<td>58.46 ± 3.59</td>
<td>1091.69 ± 131.66</td>
</tr>
<tr>
<td>3:7</td>
<td>1.96 ± 0.02</td>
<td>66.77 ± 2.95</td>
<td>1491.95 ± 132.57</td>
</tr>
</tbody>
</table>

* n1, n4 stand for [Hmim][Gly] and AMP, respectively.

Table 4  
The kinetic data for CO2 absorption in 0.3 M [Hmim][Gly] + 0.7 M AMP solution at different temperature.  

<table>
<thead>
<tr>
<th>T (K)</th>
<th>N × 10³ (mol m⁻² s⁻¹)</th>
<th>E</th>
<th>k2 (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.72 ± 0.03</td>
<td>39.67 ± 1.95</td>
<td>488.77 ± 48.19</td>
</tr>
<tr>
<td>303</td>
<td>1.76 ± 0.00</td>
<td>43.65 ± 0.28</td>
<td>587.75 ± 8.29</td>
</tr>
<tr>
<td>313</td>
<td>1.79 ± 0.03</td>
<td>49.25 ± 2.25</td>
<td>778.77 ± 71.91</td>
</tr>
<tr>
<td>323</td>
<td>1.84 ± 0.01</td>
<td>57.43 ± 1.02</td>
<td>1107.49 ± 39.20</td>
</tr>
</tbody>
</table>

* k2, E

Fig. 9. Arrenius plot of k2 for CO2-[Hmim][Gly]-AMP reaction as a function of temperature.

A second-order reaction rate constant for the reaction between CO2 and AMP was obtained from the paper (Gabrielsen et al., 2006). 

\[ k_{2,\text{AMP}} = 1.943 \times 10^{-10} \exp\left(-\frac{5176.49}{T}\right) \]  

CO2 absorption into the mixed solution had a higher absorption rate compared with that of AMP. This might attribute to the increase of the reaction rate constant. The activation energy of k2[Hmim][Gly]-AMP, k2, was 28.0, 43.0 kJ mol⁻¹, respectively. This result showed that the reactivity of AMP was significantly enhanced with an addition of [Hmim][Gly].

6. Conclusions  

A mixed solution of [Hmim][Gly]-AMP with a low viscosity, high solubility and high absorption capacity of CO2 was proposed for CO2 capture in this work. The results showed that the reactivity of AMP was significantly enhanced with the addition of [Hmim][Gly]. Moreover, CO2 absorption into the mixed solution was stable in a temperature range of 298–323 K. The optimum regeneration temperature and regeneration time of [Hmim][Gly]-AMP solution were 333 K and 60 min, respectively. The mixed system could be satisfactorily regenerated after three cycles. The study of 13C NMR spectrum indicated that CO2 reacted with [Hmim][Gly]-AMP conformed to zwitterionic mechanism. The reaction region was found to be fast pseudo-first order. Some important kinetic parameters (e.g. k2 and E) of CO2 absorption into [Hmim][Gly]-AMP solution were obtained.

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References  


