Chemical Absorption of Carbon Dioxide into Aqueous Piperazine Solutions Using a Stirred Reactor

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ABSTRACT: In this work, the absorption of CO$_2$ using aqueous piperazine (PZ) solution have been investigated both experimentally and theoretically. The absorption experiments were carried out in a stirred batch contactor with two flat blades. The experimental data are obtained over the temperature range of 298–338 K and for the PZ concentration, CO$_2$ partial pressure and the stirrer speed in the range of 0.5–1.5 kmol/m$^3$, 2.5-7.5 bar, and 0-300 rpm, respectively. The influences of each variable upon the absorption flux, removal efficiency, and loading of CO$_2$ have been investigated. In addition, a model based on chemical equilibrium in the liquid phase is employed to evaluate the concentration of chemical species in the liquid phase. Evidence suggests that CO$_2$ absorption flux, removal efficiency, and the loading increase with decreasing the temperature and increasing the stirrer speed. When PZ concentration is increased, the absorption flux and removal efficiency increase and CO$_2$ loading reduce. Also by increasing PZ concentration from 0.5 to 1.5 M at a temperature of 388 K, absorption efficiency is increased from 70 % to 95 %. CO$_2$ absorption flux was decreased from about 0.0175 to 0.01 mol/m$^2$ s when CO$_2$ loading was increased from 0.32 to 0.51.

KEYWORDS: Chemical absorption; Carbon dioxide; Piperazine solution; Stirred reactor.

INTRODUCTION

Global warming caused by the greenhouse gas emissions has received wide attention [1, 2]. Carbon dioxide (CO$_2$) is one of the main contributors to the greenhouse effect [3-5]. CO$_2$ capture includes a set of technologies that, if well implemented, would reduce greenhouse gas emissions [6, 7]. CCS (CO$_2$ capture and
storage) involves the capture of CO\textsubscript{2} from flue gases of power plants and other industrial processes [8]. A number of techniques have been developed for CO\textsubscript{2} capture including physical and chemical absorption [9-10], adsorption [11-12] and membrane [13-19]. Among the well-known technologies, chemical absorption using aqueous alkanolamine solutions as solvents will probably be the dominant technology for CO\textsubscript{2} capture [20]. Among alkanolamines, the most commonly applied solvent is monoethanolamine (MEA) that is a primary amine. Other alkanolamines also used such as diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA) and N-methyldiethanolamine (MDEA) [21-24]. Nevertheless, these traditional solvents have various disadvantages such as: oxidative degradation, low capacity of CO\textsubscript{2} loading, high regeneration energy and volatility of the primary and secondary amines, and low reaction rate of the tertiary amines [25, 26]. Consequently, a crucial step for CO\textsubscript{2} alleviation is using solvents with more reactivity, high absorption capacity and low regeneration energy. Besides mentioned amines, piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP) have also been commercially employed [27].

Piperazine (PZ), due to its high reactivity with CO\textsubscript{2}, has been employed as an efficient promoter to improve CO\textsubscript{2} capture performance [28, 29]. PZ is more effective as compared to common accelerators. The reaction rate constant of PZ with CO\textsubscript{2} is higher than conventional amines such as MEA [30]. Therefore, blended absorbents containing PZ can provide high absorption rates and grow absorption capacity and simultaneously decrease regeneration energy [31]. As shown in Table 1, solutions with various operating conditions including concentrations of PZ, temperature and pressure have been proposed as an effective stand-alone solvent for CO\textsubscript{2} absorption purposes.

As explained before, in previous literatures some examples of using PZ as a solvent for CO\textsubscript{2} absorption were studied [32-36], but here, we decided to study CO\textsubscript{2} absorption using different quantities of PZ in a stirred batch contactor with two flat blades by following procedures: a) Specifying the temperature, total pressure, initial concentration of PZ solution, and CO\textsubscript{2} loading, b) Calculation of the equilibrium constants, and c) applying the Newton-Raphson method to solve system of nonlinear algebraic equations. The main purpose of this work is to characterize the absorption of CO\textsubscript{2} into aqueous PZ solutions based on experimental data in a stirred batch reactor over the temperature range of 298-398 K and PZ concentration range of 0.5-1.5 kmol m\textsuperscript{-3}. As well, the stirrer speed and the partial pressure of CO\textsubscript{2} have been considered in the range of 0-300 rpm and 2.5-7.5 bar, respectively. Absorption rate, removal efficiency and CO\textsubscript{2} loading have been measured and effects of temperature, PZ concentration, stirrer speed and CO\textsubscript{2} partial pressure have been investigated. In addition, a vapour–liquid equilibrium model has been applied to estimate the concentrations of chemical species in the liquid phase.

**EXPERIMENTAL SECTION**

Aqueous solutions employed as absorbent have been produced using different quantities of PZ supplied by Merck. To prepare the aqueous solutions of PZ (in the range 0.5–1.5 M), bi-distilled water has been used. The gas phase contained CO\textsubscript{2} (99.99% purity) supplied by Hamate Gas Mehrabad. The experimental setup is shown schematically in Fig. 1. The inner diameter and height of the reactor were 5 cm and 9 cm, respectively. One stirrer with two flat blades with the diameter of 25 mm was used to mix liquid phase. For a typical run, 30 ml of PZ aqueous solution of the desired concentration was placed in the reactor. Then, the reactor was sealed and heated to the desired operating temperature. Once the temperature had stabilized, CO\textsubscript{2} was induced into the reactor until the desired total system pressure was reached. Then, the inlet valve was closed and the system pressure was recorded. Following the contact of CO\textsubscript{2} with the liquid phase, the total pressure of system dropped gradually and equilibrium was assumed to have been obtained when the system pressure did not change. At equilibrium, he reactor was shut down and cleared for another run. The absorption amount of CO\textsubscript{2} can be calculated by using following equation:

\[ n_{CO_2} = \frac{(P_i - P_f)V}{RTz} \]  \hspace{1cm} (1)

Which \( P_i, P_f, V, Z, n, R, T \) are initial pressure, final pressure, volume, compressibility factor, number of moles, gas constant and temperature, respectively. Then, the removal efficiency \( n_{e_{CO_2}} \) and CO\textsubscript{2} loading \( \alpha_{e_{CO_2}} \) can be obtained as below:

\[ n_{e_{CO_2}} = \frac{CO_2\ absorption\ amount\ (mol)}{CO_2\ initial\ amount\ (mol)} \]  \hspace{1cm} (2)

\[ \alpha_{e_{CO_2}} = \frac{CO_2\ loading\ (mol)}{CO_2\ initial\ loading\ (mol)} \]  \hspace{1cm} (3)
Table 1: Some examples of using PZ as a solvent for CO₂ absorption.

<table>
<thead>
<tr>
<th>Entry</th>
<th><a href="M">PZ</a></th>
<th>Pressure(atm)</th>
<th>Temperature (K)</th>
<th>Brief description</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2, 0.6</td>
<td>Total pressure 1-8 atm</td>
<td>298-313</td>
<td>Study of reaction kinetics, mass transfer and solubility Wetted wall contactor</td>
<td>The rate constant for PZ is an order of magnitude higher than primary amine MEA. Measurements of the rate constant represent true second-order intrinsic kinetics.</td>
<td>[32]</td>
</tr>
<tr>
<td>2</td>
<td>0.6-1.5</td>
<td>CO₂ partial pressure: up to 50 kPa</td>
<td>293-313</td>
<td>Reaction kinetics study Stirred cell reactor</td>
<td>The reaction between PZ and CO₂ seems to be an overall second-order reaction. It should be noted that experimental diffusivity data is necessary to finally confirm this.</td>
<td>[33]</td>
</tr>
<tr>
<td>3</td>
<td>2, 5, 8, 12</td>
<td>Total pressure: 1-6.8 atm</td>
<td>313, 333</td>
<td>Measurement of absorption and desorption rates Wetted wall contactor</td>
<td>8 m PZ has about a 75% greater CO₂ capacity than 7 m MEA. CO₂ absorption and desorption is 2-3 times faster with PZ than with MEA at equivalent CO₂ partial pressure.</td>
<td>[34]</td>
</tr>
<tr>
<td>4</td>
<td>7, 8, 9, 10</td>
<td>CO₂ partial pressure: 0.5-5 kPa</td>
<td>408-448</td>
<td>Investigation of Concentrated, aqueous PZ solution as a novel amine solvent Wetted wall contactor</td>
<td>The CO₂ absorption rate of aqueous PZ is more than double that of 7 m MEA. Thermal degradation is negligible in concentrated aqueous PZ up to 423 K (a significant advantage over MEA systems).</td>
<td>[28]</td>
</tr>
<tr>
<td>5</td>
<td>0.3-1.1</td>
<td>CO₂ partial pressure: up to 9.2 kPa</td>
<td>300-310</td>
<td>Modeling of kinetics and mass transfer rate Packed column</td>
<td>A new rigorous semi-empirical correlation to accurately model CO₂ mass transfer rate.</td>
<td>[35]</td>
</tr>
<tr>
<td>6</td>
<td>0.1-0.5</td>
<td>CO₂ partial pressure: 16-35.2 kPa</td>
<td>295.15</td>
<td>Experimental investigation Stirrer bubble column</td>
<td>Study of loading, removal efficiency, absorption flux and mass transfer coefficients at various liquid and gas flow rate, absorbent concentration, and stirrer speed.</td>
<td>[36]</td>
</tr>
</tbody>
</table>

Fig. 1: Schematic of experimental setup.
Table 2: Numeric factor level.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>T</td>
<td>298</td>
<td>318</td>
</tr>
<tr>
<td>PZ concentration (M)</td>
<td>C_{PZ}</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>CO(_2) partial pressure (bar)</td>
<td>P_{CO2}</td>
<td>2.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3: Experiments details (stirrer speed of 300 rpm).

<table>
<thead>
<tr>
<th>Run</th>
<th>T (K)</th>
<th>P_{CO2} (bar)</th>
<th>C_{PZ} (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>298</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>298</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>298</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>298</td>
<td>7.5</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>318</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>318</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>318</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>318</td>
<td>5</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>318</td>
<td>7.5</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>338</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>338</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>13</td>
<td>338</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>338</td>
<td>7.5</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>338</td>
<td>7.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\[ \alpha_{CO_2} = \frac{CO_2 \text{ absorption amount (mol)}}{PZ \text{ amount (mol)}} \]  \hspace{1cm} (3)

In order to minimize the number of experiments and obtain the optimum experimental data, response surface methodology (RSM), based on central composite design, was employed. Accordingly, the number of experiments were reduced due to factorial design. Each numeric factors included temperature, PZ concentration and CO\(_2\) partial pressure, have three levels. It should be noted that the effect of stirrer speed has investigated separately and it was found that the best absorption performance is at 300 rpm, as will be discussed later. Therefore, in the current experimental design, the stirrer speed is constant and equal to 300 rpm (Tables 2-3).

VAPR-LIQUID EQUILIBRIUM (VLE) THERMODYNAMIC MODELING

When CO\(_2\) is absorbed in the aqueous solution of PZ, numerous chemical reactions occurred in the liquid phase. The following reactions are considered in PZ solutions [37]:

Formation of bicarbonate:
\[ CO_2 + H_2O \rightleftharpoons K_{bic} \rightarrow HCO_3^- + H^+ \]  \hspace{1cm} (4)

Dissociation of bicarbonate:
The main reason for using VLE thermodynamic modeling is that the concentrations of all species are essential to kinetic analysis. At a given temperature, initial concentration of PZ solution and CO₂ loading, the equations for estimating the 11 liquid species are as follows:

\[
\begin{align*}
\text{HCO}_3^- & \xrightarrow{K_1} \text{H}^+ + \text{CO}_3^{2-} \\
\text{Autoprotolysis of water:} & \\
\text{H}_2\text{O} & \xrightarrow{K_2} \text{H}^+ + \text{OH}^- \\
\text{Protonation of piperazine:} & \\
PZ + \text{H}^+ & \xrightarrow{K_3} \text{PZH}^+ \\
& \\
\text{Diprotonation of piperazine:} & \\
PZH^+ + \text{H}^+ & \xrightarrow{K_4} \text{PZH}_2^{2+} \\
& \\
\text{Formation of piperazine carbamate:} & \\
PZ + \text{HCO}_3^- & \xrightarrow{K_5} \text{H}_2\text{O} + \text{PZCOO}^- \\
& \\
\text{Formation of piperazine dicarbamate:} & \\
PZCOO^- + \text{HCO}_3^- & \xrightarrow{K_6} \text{H}_2\text{O} + \text{PZ} (\text{COO}^-)_2 \\
& \\
\text{Formation of Protonated Piperazine carbamate:} & \\
PZCOO^- + \text{H}^+ & \xrightarrow{K_7} \text{PZH}^-'\text{COO}^- \\
& \\
\end{align*}
\]

In which \([\text{PZ}]_{\text{initial}}\) is the initial PZ concentration of aqueous solution. \([\text{PZ}]\) is the PZ concentration in the liquid phase and so on.

Overall CO₂ balance:

\[
\begin{align*}
\text{C}_\alpha [\text{PZ}]_{\text{initial}} & = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \\
& + [\text{PZCOO}^-] + 2[\text{PZ} (\text{COO}^-)_2] + [\text{PZH}^-'\text{COO}^-] \\
& + \alpha [\text{PZ}] \\
\end{align*}
\]

Electroneutrality balance:

\[
\begin{align*}
[\text{H}^+] + [\text{PZH}^+] + 2[\text{PZH}_2^{2+}] = \\
[\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \\
[\text{PZCOO}^-] + 2[\text{PZ} (\text{COO}^-)_2] \\
\end{align*}
\]
Table 4: Parameters of chemical equilibrium constants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D×10^2</th>
<th>Ex×10^5</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_1</td>
<td>1203.01</td>
<td>68359.6</td>
<td>188.444</td>
<td>-20.642</td>
<td>-47.129</td>
<td>[38]</td>
</tr>
<tr>
<td>K_2</td>
<td>175.36</td>
<td>-7230.6</td>
<td>-30.509</td>
<td>1.31478</td>
<td>-3.72805</td>
<td>[39]</td>
</tr>
<tr>
<td>K_3</td>
<td>140.932</td>
<td>-13446</td>
<td>-22.48</td>
<td>0</td>
<td>0</td>
<td>[40]</td>
</tr>
<tr>
<td>K_4</td>
<td>14.119</td>
<td>3814.44</td>
<td>0</td>
<td>-1.5096</td>
<td>0</td>
<td>[41]</td>
</tr>
<tr>
<td>K_5</td>
<td>10.113</td>
<td>2192.3</td>
<td>0</td>
<td>-1.7396</td>
<td>0</td>
<td>[41]</td>
</tr>
<tr>
<td>K_6</td>
<td>-8.635</td>
<td>3616</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>[42]</td>
</tr>
<tr>
<td>K_7</td>
<td>-3.654</td>
<td>1322.21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>[43]</td>
</tr>
<tr>
<td>K_8</td>
<td>10.025</td>
<td>3493</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Equilibrium constants as function of temperature are expressed as follows:

\[
\ln(K_x) = A + \frac{B}{T} + C\ln T + D\times T + \frac{E}{T^2}
\]

RESULTS AND DISCUSSION

In order to the characterization of CO_2 absorption, the experiments have been carried out in several aqueous PZ solutions varying the PZ concentration, partial pressure of CO_2 fed to the reactor, temperature and stirrer speed. In the following, the effect of each parameter on CO_2 absorption flux, removal efficiency and loading is discussed. Moreover, the results which were obtained by the VLE equilibrium model are presented. Table 5 shows the results for different experimental modes.

**CO_2 absorption flux**

At the beginning of the absorption process, the liquid solution was CO_2 free. Gradually, CO_2 is absorbed from gas phase into the solution, also mass transfer driving force and absorption flux are reduced (Fig. 2-5).

Fig. 2 shows experimentally computed fluxes of CO_2 during the time with variable of temperature. In this figure the concentration of PZ, CO_2 partial pressure and stirrer speed were 1.0 M, 5.0 bar and 300 rpm, respectively. When all parameters such as PZ concentration, CO_2 partial pressure and stirrer speed are constant, increasing the temperature causes the increase in absorption amount of CO_2. It is due to the fact that the kinetic rate constants and CO_2 diffusivity are increased by increasing temperature and faster reactions rates are attained. Nevertheless, the effect of temperature may be reversed, because reactive absorption of CO_2 is exothermic in nature. Thus, the optimal temperature...
Table 5: Experimental results of CO$_2$ absorption into aqueous PZ in stirred cell reactor.

<table>
<thead>
<tr>
<th>Run</th>
<th>T (K)</th>
<th>P$_{CO_2}$ (bar)</th>
<th>C$_{PZ}$ (M)</th>
<th>Stirrer speed (rpm)</th>
<th>CO$_2$ Loading (mol/mol)</th>
<th>Mass Transfer Flux (mol/m$^2$.s)</th>
<th>Removal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298</td>
<td>2.5</td>
<td>0.5</td>
<td>300</td>
<td>0.617</td>
<td>0.00156</td>
<td>68.65</td>
</tr>
<tr>
<td>2</td>
<td>298</td>
<td>2.5</td>
<td>1.5</td>
<td>300</td>
<td>0.283</td>
<td>0.00194</td>
<td>90.99</td>
</tr>
<tr>
<td>3</td>
<td>298</td>
<td>5.0</td>
<td>1.0</td>
<td>300</td>
<td>0.554</td>
<td>0.00309</td>
<td>60.28</td>
</tr>
<tr>
<td>4</td>
<td>298</td>
<td>7.5</td>
<td>0.5</td>
<td>300</td>
<td>1.017</td>
<td>0.00245</td>
<td>36.88</td>
</tr>
<tr>
<td>5</td>
<td>298</td>
<td>7.5</td>
<td>1.5</td>
<td>300</td>
<td>0.542</td>
<td>0.00474</td>
<td>58.33</td>
</tr>
<tr>
<td>6</td>
<td>318</td>
<td>2.5</td>
<td>1.0</td>
<td>300</td>
<td>0.380</td>
<td>0.00175</td>
<td>85.11</td>
</tr>
<tr>
<td>7</td>
<td>318</td>
<td>5.0</td>
<td>0.5</td>
<td>300</td>
<td>0.674</td>
<td>0.00164</td>
<td>40.35</td>
</tr>
<tr>
<td>8</td>
<td>318</td>
<td>5.0</td>
<td>1.0</td>
<td>300</td>
<td>0.564</td>
<td>0.00284</td>
<td>65.58</td>
</tr>
<tr>
<td>9</td>
<td>318</td>
<td>5.0</td>
<td>1.5</td>
<td>300</td>
<td>0.501</td>
<td>0.00348</td>
<td>85.58</td>
</tr>
<tr>
<td>10</td>
<td>318</td>
<td>7.5</td>
<td>1.0</td>
<td>300</td>
<td>0.659</td>
<td>0.00323</td>
<td>50.91</td>
</tr>
<tr>
<td>11</td>
<td>338</td>
<td>2.5</td>
<td>0.5</td>
<td>300</td>
<td>0.526</td>
<td>0.00117</td>
<td>67.62</td>
</tr>
<tr>
<td>12</td>
<td>338</td>
<td>2.5</td>
<td>1.5</td>
<td>300</td>
<td>0.260</td>
<td>0.00169</td>
<td>96.03</td>
</tr>
<tr>
<td>13</td>
<td>338</td>
<td>5.0</td>
<td>1.0</td>
<td>300</td>
<td>0.578</td>
<td>0.00264</td>
<td>71.04</td>
</tr>
<tr>
<td>14</td>
<td>338</td>
<td>7.5</td>
<td>0.5</td>
<td>300</td>
<td>0.689</td>
<td>0.00158</td>
<td>29.63</td>
</tr>
<tr>
<td>15</td>
<td>338</td>
<td>7.5</td>
<td>1.5</td>
<td>300</td>
<td>0.553</td>
<td>0.00392</td>
<td>68.05</td>
</tr>
</tbody>
</table>

Fig. 2: Changes in CO$_2$ absorption mass transfer flux with time at $P_{CO_2}$=5 bar and $C_{PZ}$=1 M and 300 rpm.

for the best absorption performance should be specified. In this work, due to exothermic chemical absorption, the CO$_2$ absorption flux is reduced with increasing the temperature.

Calculated fluxes of CO$_2$ absorption into various aqueous solutions of different concentration is illustrated in Fig. 3 at temperature of 318 K and partial pressure of 5 bar CO$_2$. It reveals that an increase in PZ concentration leads to a higher mass transfer flux. In terms of chemical dynamics, a higher absorbent concentration means the higher amount of reactant that will improve the reaction rate and the CO$_2$ absorption rate. However, a higher growth rate in CO$_2$ absorption flux occurs when the PZ concentration is low. As the amine concentration increases, the solution viscosity simultaneously increases which may result in slowing down the mass transfer in solution.

Pressure has direct effect on CO$_2$ absorption [44]. It can be seen from Fig. 4 that the mass transfer flux is increased when the CO$_2$ partial pressure increases in the gas phase. In this figure the temperature and PZ concentration were 318 K and 1 M, respectively. It is evident that at the constant temperature, amine concentration and stirrer speed, increasing in gas CO$_2$ partial pressure makes mass transfer driving force increases. In accordance with two-film theory, the rate of mass transfer is proportional to the bulk gas partial pressure. Thus, the CO$_2$ absorption flux increases promptly as its partial pressure increases.

The effect of stirrer speed on absorption flux can be observed in Fig. 5. In this case, temperature, PZ concentration and CO$_2$ partial pressure are 298 K, 1 M and 5 bar, respectively. The absorption flux of CO$_2$
increases by speeding up the stirrer from 0 to 300 rpm. Indeed, increasing speed causes more effective contact between gas and liquid phases and as a result CO₂ absorption amount increases.

**CO₂ removal efficiency**

CO₂ removal efficiency is dependent on many factors and is different in various times [45]. The determined results for the variations of CO₂ removal efficiency over time at different stirrer speeds are shown in Fig. 6. Temperature, PZ concentration and CO₂ partial pressure are equal to 298 K, 1 M and 5 bar, respectively. During the CO₂ absorption from gas to aqueous solution of PZ, the CO₂ partial pressure in the gas phase is decreased gradually until the solution is saturated and the absorption process is completed. Reduction of CO₂ partial pressure means more absorption amount in the liquid and following to Equation (2), it is equal to increasing in the absorption efficiency. As described earlier about the absorption flux, the higher stirrer speeds will produce more effective contact between phases which leads to increasing in the absorption amount and higher removal efficiency of CO₂.

Effects of PZ concentration, CO₂ partial pressure and temperature on absorption efficiency are presented in Fig. 7.

As seen in the figure, in a constant PZ concentration, CO₂ partial pressure and stirrer speed, the removal efficiency reduces with increasing the temperature. It is known that according to exothermic nature of reactive absorption, when temperature increases, equilibrium absorption capacity decreases. Also according to the Arrhenius equation, reaction rate increases. Hence, a decrease in absorption efficiency for aqueous PZ solution with temperature seemed to be more affected by a reduction in absorption capacity than by an increase in reaction rate.
Fig. 7 shows two obvious issues. First, when temperature and amine concentration are fixed, an increase in partial pressure of CO₂ causes a decrease in removal efficiency. Second, in a constant temperature and CO₂ partial pressure, the removal efficiency is increased with increasing the PZ concentration.

CO₂ loading
As mentioned, the solution was initially free from CO₂. As the absorption process begins, CO₂ loading is increased gradually and will eventually reach a constant value due to decreasing in driving force during the absorption (Fig. 8). Also, Fig. 8 shows an increase in CO₂ loading due to stirrer speed rising.

In the literature, CO₂ absorption was measured at various CO₂ loadings [34, 46]. CO₂ Absorption flux versus its loading is depicted in Fig. 9 for Run 1, 8 and 15. This figure implies a decreasing in flux with increasing in loading and this is due to reduction of the driving force by increasing the amount of CO₂ in the PZ solution.

Fig. 10 indicates that the removal efficiency of CO₂ is increased when the CO₂ loading increased. It may be justified in a constant value of PZ concentration, temperature and stirrer speed, increasing the loading is equivalent to increasing the CO₂ amount in the liquid phase and further reduction of CO₂ partial pressure in the gas phase. So, the absorption efficiency is increased directly with CO₂ loading. It should be noted that due to the reduction of absorption capacity, CO₂ loading is decreased with increasing the temperature. As well, it is evident that CO₂ loading is increased when an increase/ a decrease is occurred in the CO₂ partial pressure and PZ concentration, respectively.
Concentration of chemical species in the liquid phase

Fig. 11 shows variations in the concentration of chemical species with time for Run 1, 2, 5, and 15. By comparing the results of Run 1 and 2, Run 2 and 5, and Run 5 and 15, the influence of initial PZ concentration, CO₂ partial pressure and temperature on chemical species concentration are specified. For instance, in the case of molecular PZ and CO₂, chemical reactions are occurred as soon as the absorption of CO₂ gas in the aqueous solution of PZ. As a result of CO₂ absorption, molecular CO₂ concentration in the solution is increased directly and PZ is rapidly consumed (Fig. 11). An increase in initial PZ concentration leads to an increase in molecular PZ concentration and also a decrease in molecular CO₂ concentration. When the temperature, PZ concentration and stirrer speed are constant, increasing the CO₂ partial pressure means more reduction of PZ concentration and increasing the CO₂ concentration.

For temperature of 298 K, PZ concentration of 0.5 M and CO₂ partial pressure of 5 bar, the effect of stirrer speed on PZ and CO₂ concentration are shown in Figs. 12 and 13, respectively. PZ consumption rate when the stirrer speed increases is faster, respect to the motionless stirrer and more effective contact. Moreover, the more effective contact causes more absorption of CO₂ molecules and as a result, its concentration is increased.

Fig. 14 shows influence of stirrer on variations in the concentration of chemical species with CO₂ loading for temperature of 298 K, PZ concentration of 0.5 M and CO₂ partial pressure of 5 bar. Figs. 14 (a) and (b) are related to motionless and 300 rpm stirrer, respectively. As previously mentioned, the presence of a stirrer has a positive effect on absorption process and as shown in the figure, increasing the stirrer speed from 0 to 300 rpm leads to a significant increasing in the CO₂ loading.

Solution pH

Solution pH of CO₂-PZ-H₂O system was evaluated by applied chemical equilibrium model. The changes in pH of solution during CO₂ absorption in different conditions are shown in Fig. 15. Also, pH of aqueous solution affected by stirrer speed can be seen in Fig. 16. CO₂ absorption gradually leads to decreasing the solution pH. In other words, higher loading of CO₂ is meaning of less solution pH.

When initial PZ concentration is increased, solution pH is increased. But, an increase in CO₂ partial pressure results in a reduction of pH. Higher speed of stirrer leads to more consumption of PZ and causes the decrease in pH of solution.

CONCLUSIONS

The reactive absorption of CO₂ by aqueous PZ solution in a stirred batch reactor was studied under various conditions of temperature, amine concentration, CO₂ partial pressure and stirrer speed. Moreover, a chemical equilibrium model was applied to estimate the chemical species concentrations in the liquid phase. It was found that the temperature has negative effect on CO₂ absorption rate whereas the stirrer speed has positive effect on the absorption flux, removal efficiency. The efficiency and flux of CO₂ absorption were found to increase with increasing PZ concentration. Increasing the CO₂ partial pressure leads to increase in mass transfer flux and decrease in absorption efficiency. In addition, results show that decreasing in CO₂ absorption flux lead to increasing in CO₂ loading. The results represented that the mass transfer flux is basically controlled by the liquid phase resistance and stirrer speed and the aqueous PZ concentration have a great effect on mass transfer flux. It was also observed that the stirrer effect in high PZ concentration is more than the dilute solution. Finally, the results showed that contact time is on the important parameter in the chemical absorption system. Increasing stirrer speed will decrease the contact time of absorption process consequently mixing in liquid phase reduces liquid phase resistance for mass transfer.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>Parameter in Eq. (23)</td>
</tr>
<tr>
<td>B</td>
<td>Parameter in Eq. (23)</td>
</tr>
<tr>
<td>C</td>
<td>Parameter in Eq. (23)</td>
</tr>
<tr>
<td>CₚZ</td>
<td>PZ Concentration, mol.L</td>
</tr>
<tr>
<td>D</td>
<td>Parameter in Eq. (23)</td>
</tr>
<tr>
<td>E</td>
<td>Parameter in Eq. (23)</td>
</tr>
<tr>
<td>Kₓ</td>
<td>Equilibrium constant of reaction x</td>
</tr>
<tr>
<td>m</td>
<td>Molality, mol/kg</td>
</tr>
<tr>
<td>M</td>
<td>Molarity, mol/L</td>
</tr>
<tr>
<td>n</td>
<td>Number of moles</td>
</tr>
<tr>
<td>N</td>
<td>Absorption flux mol/m²·s</td>
</tr>
<tr>
<td>[PZ]₀</td>
<td>Initial concentration of PZ, mol.L</td>
</tr>
</tbody>
</table>
Fig. 11: Variations of chemical species concentration during the absorption process.
Fig. 12: Concentration of PZ during the absorption process at different stirrer speeds ($T=298$ K, $P_{CO_2}=5$ bar and $C_{PZ}=0.5$ M).

Fig. 13: Concentration of CO$_2$ during the absorption process at different stirrer speeds ($T=298$ K, $P_{CO_2}=5$ bar and $C_{PZ}=0.5$ M).

Fig. 14: Variations of chemical species concentration with CO$_2$ loading (298 K, 5 bar, and 0.5 M) at different stirrer speeds (a) 0 and (b) 300 rpm.

Fig. 15: Solution pH during absorption process in various conditions.

Fig. 16: Influence of stirrer speed on solution pH for 298 K, 0.5 M and 5 bar.
P
PCO2
R
T
V
Z
Greek symbols
α
η
Amine abbreviations
AMP
DEA
DIPA
MDEA
MEA
PZ
TEA

Pressure, Pa
CO2 partial pressure, bar
Gas constant, m3.Pa/K.mol
Temperature, K
Volume, m3
Compressibility factor
Loading, mol/mol
Removal efficiency, %
2-amino-2-methyl-1-propanol
Diethanolamine
Disopropanolamine
N-Methyl diethanolamine
Monoethanolamine
Piperazine
Triethanolamine

REFERENCES


