Experimental Study of CO₂ Absorption in Different Blend Solutions as Solvent for CO₂ Capture

Rouzbeh Ramezani, Renzo Di Felice

Abstract—Nowadays, removal of CO₂ as one of the major contributors to global warming using alternative solvents with high CO₂ absorption efficiency, is an important industrial operation. In this study, three amines, including 2-methylpiperazine, potassium sarcosinate and potassium lysinate as potential additives, were added to the potassium carbonate solution as a base solvent for CO₂ capture. In order to study the absorption performance of CO₂ in terms of loading capacity of CO₂ and absorption rate, the absorption experiments in a blend of additives with potassium carbonate were carried out using the vapor-liquid equilibrium apparatus at a temperature of 313.15 K, CO₂ partial pressures ranging from 0 to 50 kPa and at mole fractions 0.2, 0.3, and 0.4. Furthermore, the performance of CO₂ absorption in these blend solutions was compared with pure monoethanolamine and with pure potassium carbonate. Finally, a correlation with good accuracy was developed using the nonlinear regression analysis in order to predict CO₂ loading capacity.

Keywords—Absorption rate, carbon dioxide, CO₂ capture, global warming, loading capacity.

I. INTRODUCTION

CARBON dioxide as one of the most important greenhouse gases is currently responsible for over 60% of the global warming impact [1]. Thus, CO₂ absorption from industrial activities such as power plant flue gas streams is essential in order to decrease greenhouse gas effect. One of the most attractive technologies for post-combustion carbon dioxide absorption is chemical absorption into liquid solvent such as alkanolamines [2]. However, alkanolamines have disadvantages such as the low loading capacity of CO₂, high regeneration energy, oxidative degradation, and higher corrosion rate. Therefore, the search for an alternative solvent with better absorption efficiency has gained recent interests in research [3]. Many researchers used solvent blend systems with different advantages as an excellent technique to produce absorbers with better absorption performance for CO₂ capture. Hamzehie and Najibi [4] measured CO₂ solubility in solution of 2-amino-2-methyl-1-propanol (AMP) blended with potassium prolinate using a vapor liquid equilibrium cell at partial pressure of CO₂ up to 2583 kPa and temperatures 293.15 and 323.15 K. The results indicated that with increase in concentration of potassium prolinate, CO₂ loading capacity of blend solution decreases. Haghtalab and Ghahremani [5] used mixture of methyldiethanolamine (MDEA) + AMP + 2-piperazine (PZ) as a solvent for CO₂ absorption at temperatures and CO₂ partial pressures ranging between (313.15 and 343.15 K) and from 1 to 40 bars, respectively. They concluded that CO₂ solubility increases with increasing the PZ/AMP ratio. Lee et al. [6] added potassium glycinate as a promoter to potassium carbonate in order to increase the absorption rate performance at temperature ranging from 323 to 343 K. The obtained results showed that addition of potassium glycinate to potassium carbonate can increase absorption rate of CO₂. Kang et al. [7] reported solubility of CO₂ in blend of PZ and potassium alaninate at temperatures of 313.15 K and 353.15 K. They observed that CO₂ loading capacity decreases with increasing temperature. Shen et al. [8] suggested arginine as an activator into aqueous potassium carbonate solution at temperature ranging from 313 to 343 K. It was found that CO₂ absorption rate in blend solution increased with increase of concentration of arginine. Muraleedharan et al. [9] investigated effect of addition of monoethanolamine (MEA) on CO₂ absorption rate in 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) at different temperature. The obtained results revealed that CO₂ absorption rate increases when the monoethanolamine concentration increases in the solution. Mazinani et al. [10] studied CO₂ loading capacity in sodium glycinate + monoethanolamine system at pressures up to 35 kPa using stirred batch reactor. They indicated that sodium glycinate has a positive effect on loading capacity. Balsora and Mondal [11] evaluated CO₂ absorption performance in a blend of diethanolamine and trisodium phosphate and concluded that with increasing mole fraction of trisodium phosphate, loading capacity increases. Yang et al. [12] determined new experimental data of CO₂ loading capacity in mixture of AMP and PZ at temperatures of 313, 333, and 353 K. Their results showed that PZ+AMP can be selected as a good solvent with high loading capacity for CO₂ capture. Chung et al. [2] examined CO₂ solubility in blend of triethanolamine (TEA) and PZ at pressures up to 153 kPa and observed that TEA+PZ solution has higher capacity in comparison with pure TEA.

Few inorganic absorbents such as potassium carbonate (K₂CO₃) indicated a good performance for CO₂ capture in comparison with alkanolamines in terms of corrosiveness, regeneration energy and toxicity [13]. However, the main challenge of potassium carbonate is low reactivity with CO₂. Thus, in this study, three amine additives, including 2-methylpiperazine (2MPZ), potassium sarcosinate (K-Sar) and potassium lysinate (K-Lys) as potential additives were added.
to K$_2$CO$_3$ in order to increase the CO$_2$ absorption performance. The absorption rate and loading capacity of CO$_2$ in these blended solutions were measured at 313.15 K, CO$_2$ partial pressure up to 50 kPa and at additive mole fractions 0.2, 0.3, and 0.4 using the equilibrium reactor. Furthermore, the absorption performance was compared with pure MEA and pure K$_2$CO$_3$. The objective of this study is to introduce a new solvent with high CO$_2$ absorption from flue gases.

II. REACTION MECHANISM

A. Reaction CO$_2$ with K$_2$CO$_3$

Sherier and Danckwerts [14] observed that the absorption rate of CO$_2$ increase with addition of amine promotors according with following equations:

$CO_2 + $ Promoter $\leftrightarrow$ Intermediate

Intermediate $+$ OH$^- \leftrightarrow HCO$_2^-$ $+$ Promoter

$K_2CO_3 + H_2O$ $\leftrightarrow 2K^+ + HCO_3^- + OH^-$

$2H_2O$ $\leftrightarrow H_2O^+$ $+$ OH$^-$

$OH^- + CO_2 \leftrightarrow HCO_3^-$

$HCO_3^- + OH^- \leftrightarrow CO_2^{2-} + H_2O$

B. Reaction CO$_2$ with 2-MPZ

Kim et al. [15] indicated the reaction mechanism of 2-MPZ could be similar to piperazine.

$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$

$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_2^{2-}$

$2MPZ + H_2O \leftrightarrow PZH^+ + OH^-$

$2MPZH^+ + H_2O \leftrightarrow 2MPZ + H_3O^+$

$2MPZ + CO_2 + H_2O \leftrightarrow 2MPZCOO^- + H_3O^+$

$2MPZH^+ + H_2O + CO_2 \leftrightarrow H^+2MPZCOO^- + H_3O^+$

$H^+2MPZCOO^- + H_2O \leftrightarrow 2MPZCOO^- + H_3O^+$

$2MPZCOO^- + CO_2 + H_2O \leftrightarrow 2MPZ(COO^-)2 + H_3O^+$

C. Reaction CO$_2$ with K-Sar

Aronu et al. [16] showed that reaction mechanism of carbon dioxide with potassium sarcosinate can be seen at (15)-(18):

$Sar + H_3O^+ \leftrightarrow Sar^+ + H_2O$

$H_2O + Sar^+ \leftrightarrow H_3O^+ + Sar^-$

$H_2O + Sar^- \leftrightarrow H_3O^+ + Sar^-$

$H_2O + Sar^- \leftrightarrow H_3O^+ + HCO_3^-$

D. Reaction CO$_2$ with K-Lys

Shen et al. [17] concluded that the reaction mechanism of carbon dioxide with potassium lysinate can be represented based on zwitterion mechanism:

$CO_2 + H_2N - CHR - COO^+ + H_2O \leftrightarrow COO^+H_2N - CHR - COOK^+$

$C - COOH - CHR - COO^+ - K^+ + B \leftrightarrow COOH - CHR - COO - K^+ + BH^+$

III. EXPERIMENTAL SECTION

A. Materials

Table I shows a detailed of all used chemical materials in this study.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Source</th>
<th>Purity</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium carbonate</td>
<td>Merck</td>
<td>≥ 99 %</td>
<td>K$_2$CO$_3$</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>Merck</td>
<td>≥ 98 %</td>
<td>KOH</td>
</tr>
<tr>
<td>Lysine</td>
<td>Merck</td>
<td>≥ 99 %</td>
<td>Lys</td>
</tr>
<tr>
<td>Sarcosine</td>
<td>Merck</td>
<td>≥ 99 %</td>
<td>Sar</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>Merck</td>
<td>≥ 99 %</td>
<td>MEA</td>
</tr>
<tr>
<td>2-methylpiperazine</td>
<td>Merck</td>
<td>≥ 99 %</td>
<td>2-MPZ</td>
</tr>
</tbody>
</table>

B. Solubility of CO$_2$

Fig. 1 shows a schematically of vapor-liquid equilibrium which including of temperature and pressure sensor, gas cylinders, gas storage tank, water bath, and equilibrium cell. Firstly, equilibrium cell was put into water bath in order to guarantee isothermal conditions during the measurements. After that, a known amount of absorbent was charged into the reactor. The vapor pressure was recorded when pressure in reactor was stayed constant. Then, carbon dioxide was entered from gas storage tank to reactor. The total mole of carbon dioxide ($n_{CO_2}$) is obtained from:

$n_{CO_2} = \frac{V_a}{R T} \left[ \frac{P_1}{Z_1} - \frac{P_2}{Z_2} \right]$ (21)

where $P_1$, $P_2$, $V_a$, $Z_1$, $Z_2$ are initial and final pressure, gas storage tank volume, compressibility factors of CO$_2$, respectively. The moles of CO$_2$ in the gas phase, $n^g_{CO_2}$ can be obtained:

$n^g_{CO_2} = \frac{V^g_{E} \cdot n^g_{CO_2}}{R T}$ (22)

where $V^g_{E}$, $P^g_{E}$ are the volume of gas and equilibrium pressure, respectively. Thus, loading capacity of carbon dioxide is defined as:

$\alpha_{CO_2} = \frac{n_{CO_2} - n^g_{CO_2}}{n_{solvent}}$ (23)
IV. RESULTS AND DISCUSSION

A. Primary-Reliability Test

Prior to the measurement of loading capacity of carbon dioxide in the concerned absorbent systems, the loading capacity of CO\textsubscript{2} in 2.5 mol/l monoethanolamine solution at temperature of T=313.15 K was determined in order to ensure that the applied method is acceptable. Fig. 2 shows a comparison between the results of our loading capacity measurements in this study with the available data from the other publications [18]-[20].

![Fig. 2 Loading capacity of CO\textsubscript{2} in 2.5 kmol/m\textsuperscript{3} MEA solution](image)

B. Absorption of CO\textsubscript{2} in Blend Solutions

Loading capacity of CO\textsubscript{2} was measured using equilibrium cell for blend of potassium carbonate with amine additives at temperature 313.15 K, additive mole fractions 0.2, 0.3, and 0.4 and carbon dioxide partial pressures up to 50 kPa. The absorption performance of carbon dioxide was also compared with the pure potassium carbonate and pure monoethanolamine (MEA). Figs. 3 (a)-(c) indicates a representative trend of the general behavior of the obtained experimental results. As shown in Fig. 3, solubility of carbon dioxide in these blended solutions increases with increasing partial pressure of carbon dioxide. Also, it is clear that K\textsubscript{2}CO\textsubscript{3}+K-Lys system has the highest CO\textsubscript{2} loading capacity, and K\textsubscript{2}CO\textsubscript{3}+K-Sar indicated the lowest loading capacity among additives. However, further comparison with monoethanolamine shows that all the blend solutions selected have better CO\textsubscript{2} loading capacity than MEA.

The CO\textsubscript{2} loading capacity data obtained were correlated as a function of additive mole fraction (R), partial pressure of carbon dioxide (P), and temperature (T) using the nonlinear regression analysis. Results indicated that the model applied has a good agreement in predicting the solubility of CO\textsubscript{2} into blend of three additives and potassium carbonate as shown in Fig. 4.
Fig. 3 The CO₂ solubility in different blend solutions at various mole fractions, (a) 0.2, (b) 0.3, (c) 0.4: ▲, K₂CO₃+2MPZ; ●, K₂CO₃+K-Lys; ■, K₂CO₃+K-Sar; ○, K₂CO₃; □, MEA.

Fig. 4 Predicted loading capacity of CO₂ versus experimental data. The overall average absolute deviation (AAD) for systems of K₂CO₃+K-Sar, K₂CO₃+2MPZ, and K₂CO₃+K-Lys was 1.32%, 0.93%, and 0.98%, respectively. Table II presents the values of constant coefficients in (24).

\[
\text{CO}_2 \text{ Solubility} = a_0 + a_1 T + a_2 P + a_3 R + a_4 T \times P + a_5 T \times R + a_6 P \times R + a_7 T^2 + a_8 P^2 + a_9 R^2 \]  \hspace{1cm} (24)

<table>
<thead>
<tr>
<th>Co.</th>
<th>K₂CO₃+2MPZ</th>
<th>K₂CO₃+K-Lys</th>
<th>K₂CO₃+K-Sar</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₀</td>
<td>0.80323</td>
<td>2.65243</td>
<td>-0.77631</td>
</tr>
<tr>
<td>a₁</td>
<td>-0.00716739</td>
<td>-2.84098×10⁻³</td>
<td>0.017432</td>
</tr>
<tr>
<td>a₂</td>
<td>3.14567×10⁻⁴</td>
<td>-4.05337×10⁻³</td>
<td>-0.012271</td>
</tr>
<tr>
<td>a₃</td>
<td>-3.40862</td>
<td>-4.08312</td>
<td>-1.56561</td>
</tr>
<tr>
<td>a₄</td>
<td>3.88158×10⁻⁵</td>
<td>4.21053×10⁻⁵</td>
<td>5.98684×10⁻⁵</td>
</tr>
<tr>
<td>a₅</td>
<td>0.013125</td>
<td>0.01375</td>
<td>4.12500×10⁻⁵</td>
</tr>
<tr>
<td>a₆</td>
<td>-0.001329</td>
<td>-7.89474×10⁻⁵</td>
<td>4.40789×10⁻⁵</td>
</tr>
<tr>
<td>a₇</td>
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<td>-1.62750×10⁻³</td>
<td>-4.14822×10⁻⁵</td>
</tr>
<tr>
<td>a₈</td>
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<td>-8.02779×10⁻⁵</td>
<td>-5.94702×10⁻⁵</td>
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<tr>
<td>a₉</td>
<td>0.16122</td>
<td>0.79701</td>
<td>-0.32822</td>
</tr>
</tbody>
</table>

The loading capacity versus time curves for the different systems tested at temperature 313.15 K are shown in Figs. 5 (a)-(c) in order to compare initial absorption rate of carbon dioxide. It was found that the increase in additive concentration increases the absorption rate in potassium carbonate solution. Also, K₂CO₃+2MPZ solution showed the best performance in terms of CO₂ absorption rate, while K-Sar indicated least effect on absorption rate.

V. CONCLUSION

In this work, different amine additives such as 2MPZ, K-Lys, and K-Sar were added to potassium carbonate solution in order to improve carbon dioxide absorption performance in terms of carbon dioxide loading capacity and absorption rate.
using equilibrium cell at 313.15 K and pressure up to 50 kPa. Moreover, an equation with high agreement correlated the obtained CO\textsubscript{2} solubility. It was found that absorption rate in potassium carbonate increases with addition amine additive. Also, potassium lysinate and 2-methylpiperazine showed a positive impact on loading capacity.

REFERENCES


