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Experimental Study of CO_2 Absorption in Different Blend Solutions as Solvent for CO_2 Capture

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***Abstract*—**Nowadays, removal of CO_2 as one of the major contributors to global warming using alternative solvents with high CO_2 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 CO_2 capture. In order to study the absorption performance of CO_2 in terms of loading capacity of CO_2 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, CO_2 partial pressures ranging from 0 to 50 kPa and at mole fractions 0.2, 0.3, and 0.4. Furthermore, the performance of CO_2 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 CO_2 loading capacity.

***Keywords*—**Absorption rate, carbon dioxide, CO_2 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, CO_2 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 CO_2, 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 absorbents with better absorption performance for CO_2 capture. Hamzehie and Najibi [4] measured CO_2 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 CO_2 up to 2583 kPa and temperatures 293.15 and 323.15 K. The results indicated that with increase in concentration of potassium prolinate, CO_2 loading capacity of blend solution decreases. Haghtalab and Ghahremani [5] used mixture of methyldiethanolamine (MDEA) + AMP + piperazine (PZ) as a solvent for CO_2 absorption at temperatures and CO_2 partial pressures ranging between (313.15 and 343.15 K) and from 1 to 40 bars, respectively. They concluded that CO_2 solubility increases with increasing the PZ/AMP ratio. Lee et al. [6] added potassium glycinate as a promotor 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 CO_2. Kang et al. [7] reported solubility of CO_2 in blend of PZ and potassium alaninate at temperatures of 313.15 K and 353.15 K. They observed that CO_2 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 CO_2 absorption rate in blend solution increased with increase of concentration of arginine. Muraleedharan et al. [9] investigated effect of addition of monoethanolamine (MEA) on CO_2 absorption rate in 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) at different temperature. The obtained results revealed that CO_2 absorption rate increases when the monoethanolamine concentration increases in the solution. Mazinani et al. [10] studied CO_2 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 CO_2 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 CO_2 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 CO_2 capture. Chung et al. [2] examined CO_2 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 (K_2CO_3) indicated a good performance for CO_2 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 CO_2. 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

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to K_2CO_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_2CO_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_2CO_3

Sherier and Danckwerts [14] observed that the absorption rate of CO_2 increase with addition of amine promotors according with following equations:

$$CO_2 + Promoter \leftrightarrow Intermediate \quad (1)$$

$$Intermediate + OH^- \leftrightarrow HCO_3^- + Promoter \quad (2)$$

$$K_2CO_3 + H_2O \leftrightarrow 2K^+ + HCO_3^- + OH^- \quad (3)$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad (4)$$

$$OH^- + CO_2 \leftrightarrow HCO_3^- \quad (5)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (6)$$

B. Reaction CO_2 with 2-MPZ

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

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \quad (7)$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \quad (8)$$

$$2MPZ + H_2O \leftrightarrow PZH^+ + OH^- \quad (9)$$

$$2MPZH^+ + H_2O \leftrightarrow 2MPZ + H_3O^+ \quad (10)$$

$$2MPZ + CO_2 + H_2O \leftrightarrow 2MPZCOO^- + H_3O^+ \quad (11)$$

$$2MPZH^+ + H_2O + CO_2 \leftrightarrow H^+2MPZCOO^- + H_3O^+ \quad (12)$$

$$H^+2MPZCOO^- + H_2O \leftrightarrow 2MPZCOO^- + H_3O^+ \quad (13)$$

$$2MPZCOO^- + CO_2 + H_2O \leftrightarrow 2MPZ(COO^-)_2 + H_3O^+ \quad (14)$$

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):

$$Sar + H_3O^+ \leftrightarrow Sar^+ + H_2O \quad (15)$$

$$H_2O + Sar^+ \leftrightarrow H_3O^+ + Sar^- \quad (16)$$

$$H_2O + Sar^- \leftrightarrow H_3O^+ + Sar^- \quad (17)$$

$$H_2O + SarCOO^{2-} \leftrightarrow Sar^- + HCO_3^- \quad (18)$$

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:

$$CO_2 + H_2N - CHR - COOK^+ \leftrightarrow COO^+H_2N - CHR - COOK^+ \quad (19)$$

$$C - OO^+H_2N - CHR - COO^+ - K^+ + B \leftrightarrow COOHN - CHR - COO - K^+ + BH^+ \quad (20)$$

III. Experimental Section

A. Materials

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

TABLE I
Description of Chemical Materials Used in This Study

Chemical name	Source	Purity	Abbreviation
Potassium carbonate	Merck	≥ 99 %	K_2CO_3
Potassium hydroxide	Merck	≥ 98 %	KOH
Sarcosine	Merck	≥ 99 %	Sar
2-methylpiperazine	Merck	≥ 99 %	2-MPZ
Monoethanolamine	Merck	≥ 99 %	MEA
L-Lysine	Merck	≥ 99 %	Lys

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:

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

where P_1, P_2, V_b, 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, $n_{CO_2}^g$ can be obtained:

$$n_{CO2}^g = \frac{V_c^g\, P_{CO2}^e}{R\,T} \quad (22)$$

where V_c^g, P_{CO2}^e are the volume of gas and equilibrium pressure, respectively. Thus, loading capacity of carbon dioxide is defined as:

$$\alpha_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^g}{n_{solvent}} \quad (23)$$

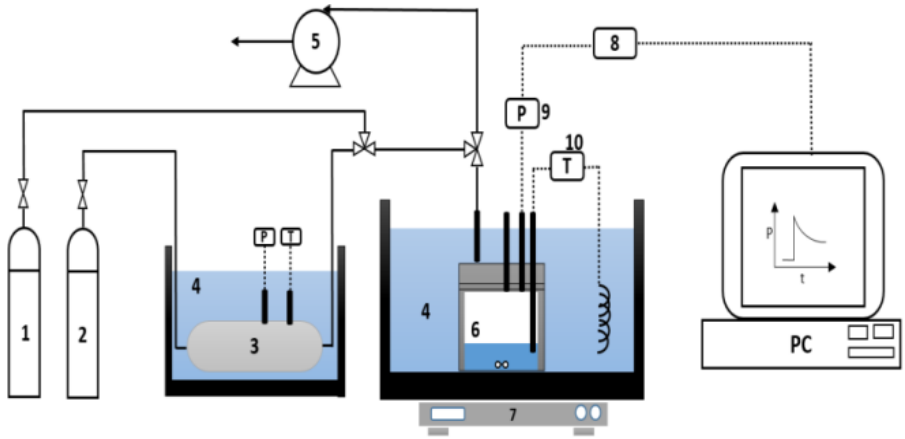


Fig. 1 Schematic of the VLE experimental setup: (1) N_2 gas cylinder; (2) CO_2 gas cylinder; (3) gas storage tank; (4) water bath; (5) vacuum pump; (6) equilibrium cell; (7) magnetic stirrer; (8) data logger; (9) pressure sensor; (10) temperature sensor

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_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].

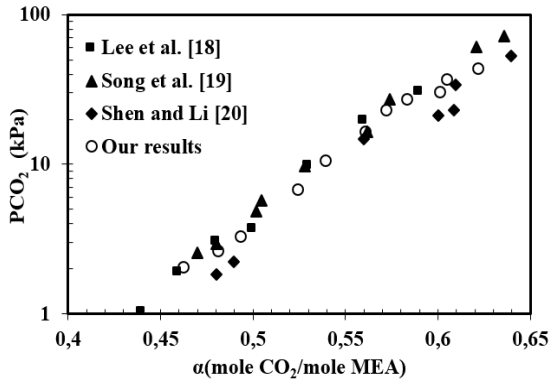
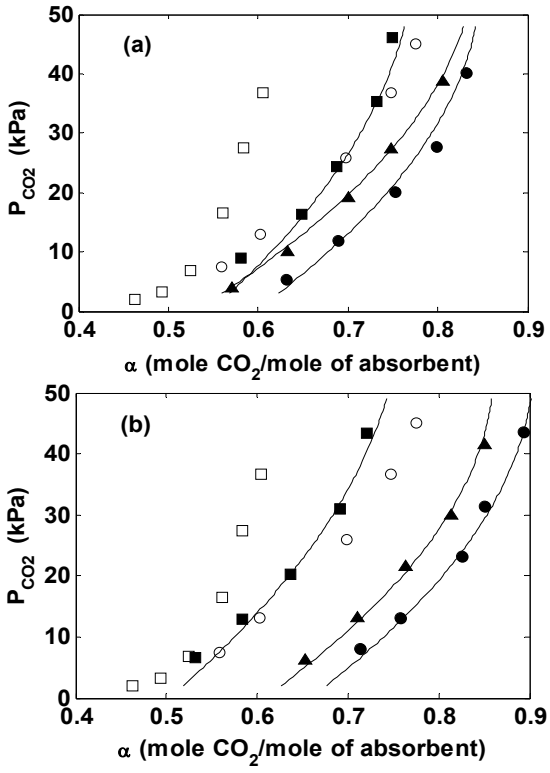


Fig. 2 Loading capacity of CO_2 in 2.5 kmol/m^3 MEA solution

B. Absorption of CO_2 in Blend Solutions

Loading capacity of CO_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_2CO_3+K-Lys system has the highest CO_2 loading capacity, and K_2CO_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_2 loading capacity than MEA.

The CO_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_2 into blend of three additives and potassium carbonate as shown in Fig. 4.



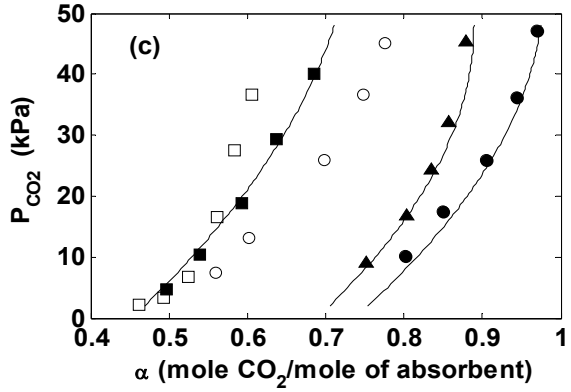


Fig. 3 The CO_2 solubility in different blend solutions at various mole fractions, (a) 0.2, (b) 0.3, (c) 0.4: ▲, K_2CO_3+2MPZ; ●, K_2CO_3+K-Lys; ■, K_2CO_3+K-Sar; ○, K_2CO_3; □, MEA

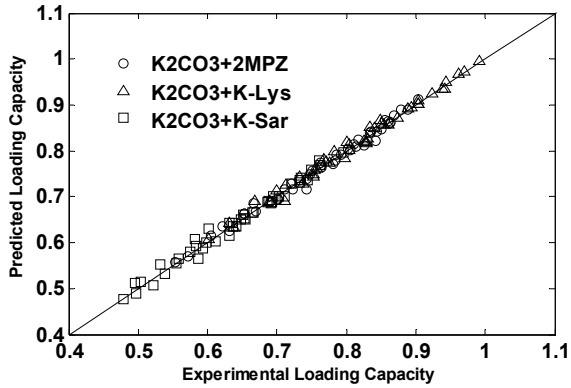


Fig. 4 Predicted loading capacity of CO_2 versus experimental data

The overall average absolute deviation (AAD) for systems of K_2CO_3+K-Sar, K_2CO_3+2MPZ, and K_2CO_3+K-Lys was 1.32%, 0.93%, and 0.98%, respectively. Table II presents the values of constant coefficients in (24).

$$CO_2 \text{ Solubility} = a_0 + a_1 T + a_2 P + a_3 R + a_4 T \times P + a_5 T \times R + a_6 P \times R + a_7 T^2 + a_8 P^2 + a_9 R^2 \quad (24)$$

TABLE II
THE VALUES OF CONSTANT COEFFICIENTS

Co.	K_2CO_3+2MPZ	K_2CO_3+K-Lys	K_2CO_3+K-Sar
a_0	0.80323	2.65243	-0.77631
a_1	0.00716739	-2.84098×10^{-3}	0.017432
a_2	3.14567×10^{-4}	-4.05337×10^{-3}	-0.012271
a_3	-3.40862	-4.08312	-1.56561
a_4	3.88158×10^{-5}	4.21053×10^{-5}	5.98684×10^{-5}
a_5	0.013125	0.01375	4.12500×10^{-3}
a_6	-0.010329	-7.89474×10^{-4}	4.40789×10^{-3}
a_7	-2.71797×10^{-5}	-1.26750×10^{-5}	-4.14822×10^{-5}
a_8	-8.66948×10^{-5}	-8.02779×10^{-5}	-5.94702×10^{-5}
a_9	0.16122	0.79701	-0.32822

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, K_2CO_3+2MPZ solution showed the best performance in terms of CO_2 absorption rate, while K-Sar indicated least effect on absorption rate.

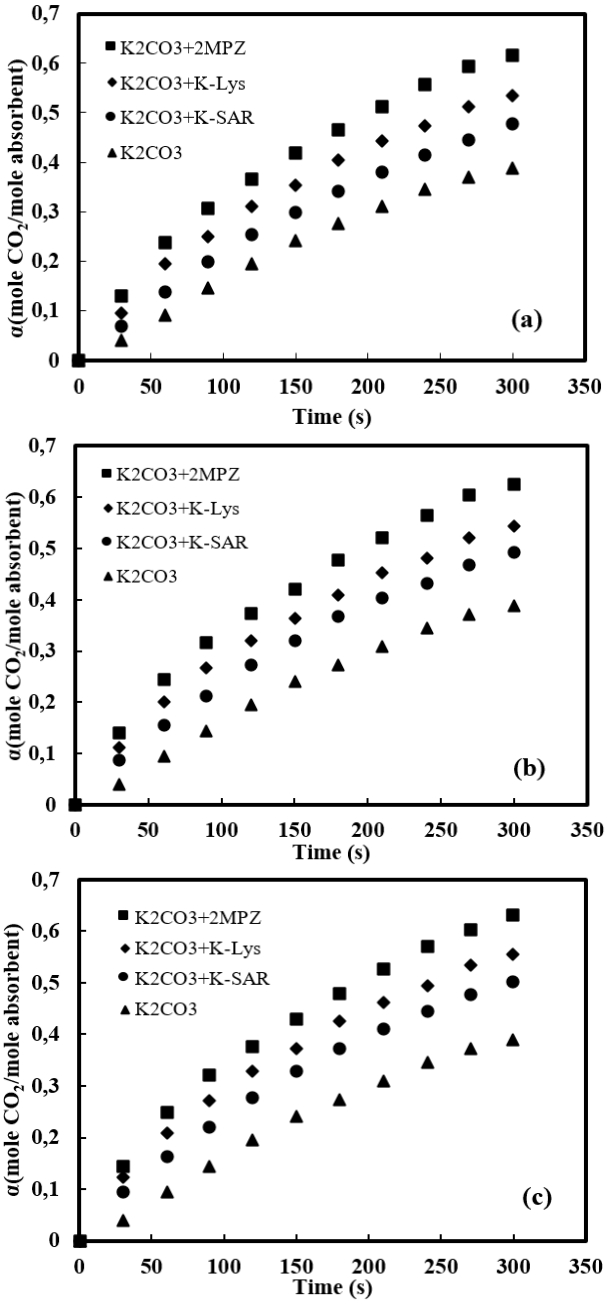


Fig. 5 Comparison of absorption rate in different mole fractions, (a) 0.2, (b) 0.3, (c) 0.4

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_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.

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