

# Experimental Study of CO<sub>2</sub> Absorption in Different Blend Solutions as Solvent for CO<sub>2</sub> Capture

Rouzbeh Ramezani, Renzo Di Felice

**Abstract**—Nowadays, removal of CO<sub>2</sub> as one of the major contributors to global warming using alternative solvents with high CO<sub>2</sub> 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<sub>2</sub> capture. In order to study the absorption performance of CO<sub>2</sub> in terms of loading capacity of CO<sub>2</sub> 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<sub>2</sub> partial pressures ranging from 0 to 50 kPa and at mole fractions 0.2, 0.3, and 0.4. Furthermore, the performance of CO<sub>2</sub> 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<sub>2</sub> loading capacity.

**Keywords**—Absorption rate, carbon dioxide, CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> capture. Hamzehie and Najibi [4] measured CO<sub>2</sub> solubility in solution of 2-amino-2-methyl-1-propanol (AMP) blended with potassium proline using a vapor liquid equilibrium cell at partial pressure of CO<sub>2</sub> up to 2583 kPa and temperatures 293.15 and 323.15 K. The results indicated that with increase in concentration of potassium proline, CO<sub>2</sub> loading capacity

of blend solution decreases. Haghtalab and Ghahremani [5] used mixture of methyldiethanolamine (MDEA) + AMP + piperazine (PZ) as a solvent for CO<sub>2</sub> absorption at temperatures and CO<sub>2</sub> partial pressures ranging between (313.15 and 343.15 K) and from 1 to 40 bars, respectively. They concluded that CO<sub>2</sub> 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<sub>2</sub>. Kang et al. [7] reported solubility of CO<sub>2</sub> in blend of PZ and potassium alaninate at temperatures of 313.15 K and 353.15 K. They observed that CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> absorption rate in 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) at different temperature. The obtained results revealed that CO<sub>2</sub> absorption rate increases when the monoethanolamine concentration increases in the solution. Mazinani et al. [10] studied CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> capture. Chung et al. [2] examined CO<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>) indicated a good performance for CO<sub>2</sub> 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<sub>2</sub>. 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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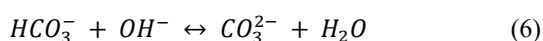
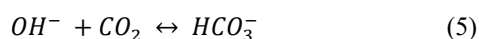
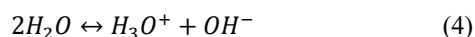
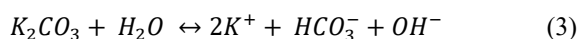
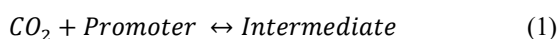
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to  $K_2CO_3$  in order to increase the  $CO_2$  absorption performance. The absorption rate and loading capacity of  $CO_2$  in these blended solutions were measured at 313.15 K,  $CO_2$  partial pressure up to 50 kPa and at additive mole fractions 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

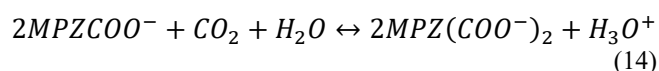
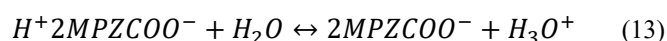
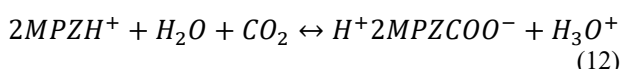
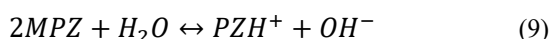
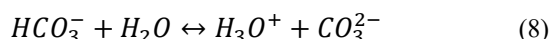
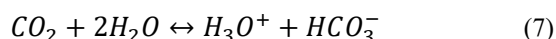
### A. Reaction $CO_2$ with $K_2CO_3$

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



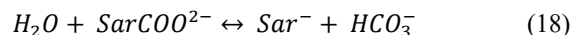
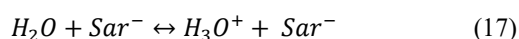
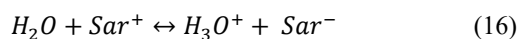
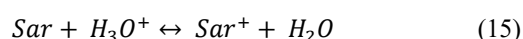
### B. Reaction $CO_2$ with 2-MPZ

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



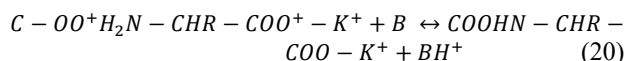
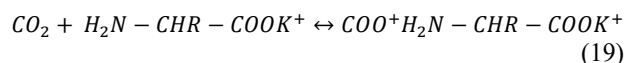
### C. Reaction $CO_2$ with K-Sar

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



### 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:



## III. EXPERIMENTAL SECTION

### A. Materials

Table I shows a detailed of all used chemical materials 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:

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

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:

$$n_{CO_2}^g = \frac{V_c^g P_{CO_2}^e}{RT} \quad (22)$$

where  $V_c^g$ ,  $P_{CO_2}^e$  are the volume of gas and equilibrium pressure, respectively. Thus, loading capacity of carbon dioxide is defined as:

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

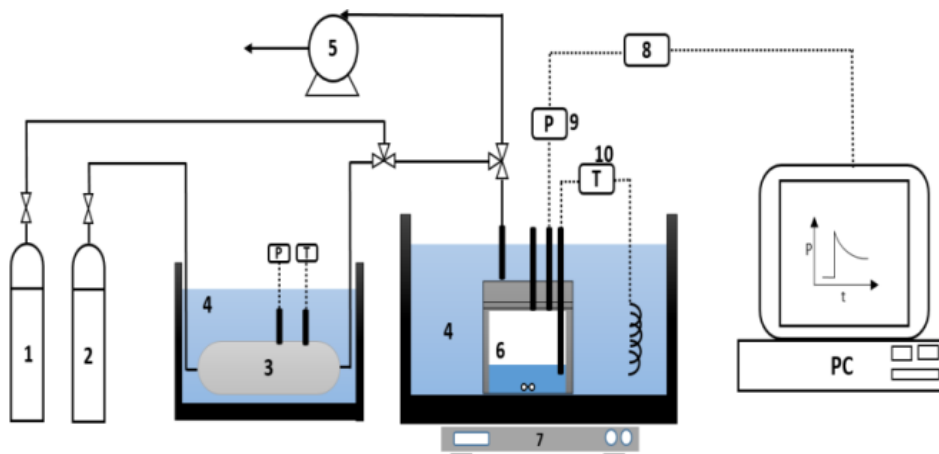


Fig. 1 Schematic of the VLE experimental setup: (1) N<sub>2</sub> gas cylinder; (2) CO<sub>2</sub> gas cylinder; (3) gas storage tank; (4) water bath; (5) vacuum pump; (6) equilibrium cell; (7) magnetic stirrer; (8) data logger; (9) pressure sensor; (10) temperature sensor

#### 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<sub>2</sub> 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].

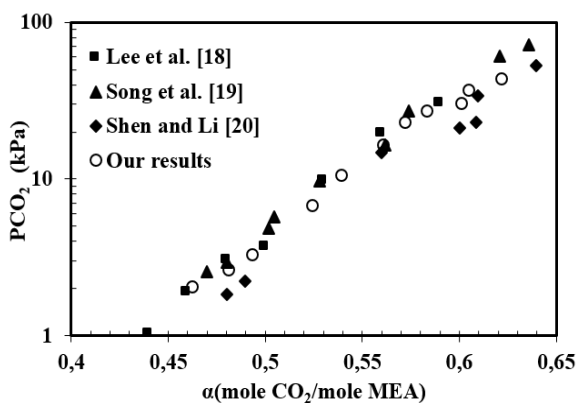


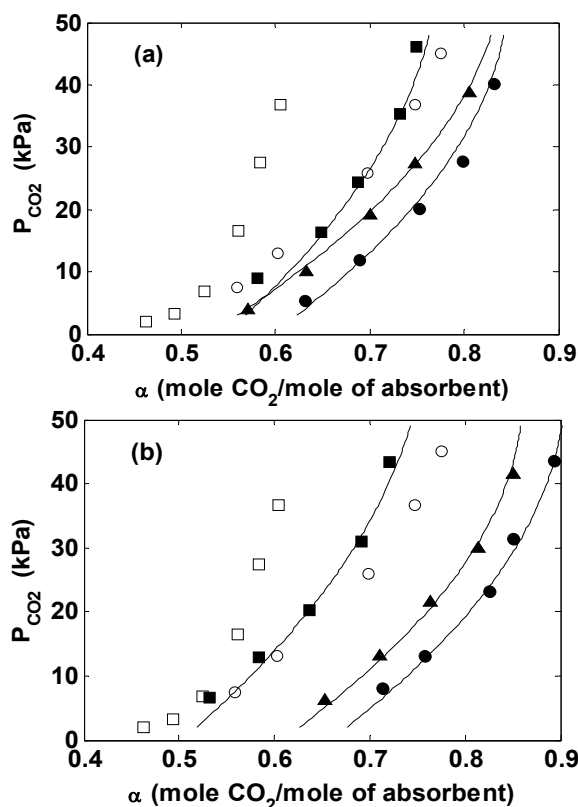
Fig. 2 Loading capacity of CO<sub>2</sub> in 2.5 kmol/m<sup>3</sup> MEA solution

##### B. Absorption of CO<sub>2</sub> in Blend Solutions

Loading capacity of CO<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>+K-Lys system has the highest CO<sub>2</sub> loading capacity,

and K<sub>2</sub>CO<sub>3</sub>+K-Sar indicated the lowest loading capacity among additives. However, further comparison with monoethanolamine shows that all the blend solutions selected have better CO<sub>2</sub> loading capacity than MEA.

The CO<sub>2</sub> 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<sub>2</sub> into blend of three additives and potassium carbonate as shown in Fig. 4.



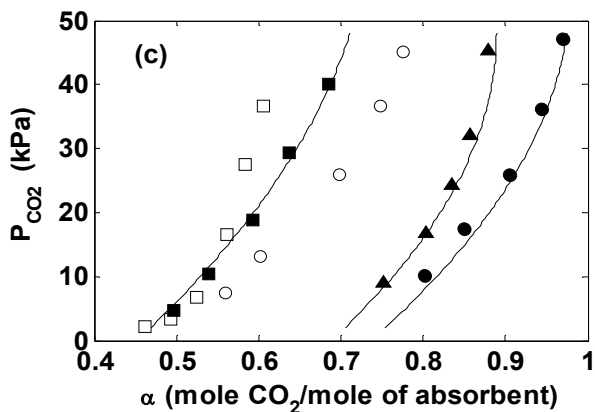


Fig. 3 The CO<sub>2</sub> solubility in different blend solutions at various mole fractions, (a) 0.2, (b) 0.3, (c) 0.4: ▲, K<sub>2</sub>CO<sub>3</sub>+2MPZ; ●, K<sub>2</sub>CO<sub>3</sub>+K-Lys; ■, K<sub>2</sub>CO<sub>3</sub>+K-Sar; ○, K<sub>2</sub>CO<sub>3</sub>; □, MEA

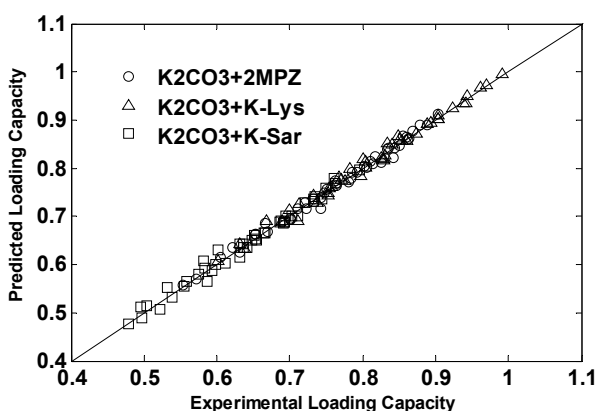


Fig. 4 Predicted loading capacity of CO<sub>2</sub> versus experimental data

The overall average absolute deviation (AAD) for systems of K<sub>2</sub>CO<sub>3</sub>+K-Sar, K<sub>2</sub>CO<sub>3</sub>+2MPZ, and K<sub>2</sub>CO<sub>3</sub>+K-Lys was 1.32%, 0.93%, and 0.98%, respectively. Table II presents the values of constant coefficients in (24).

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

| TABLE II<br>THE VALUES OF CONSTANT COEFFICIENTS |                                      |                                       |                                       |
|---|--------------------------------------|---------------------------------------|---------------------------------------|
| Co.   | K <sub>2</sub> CO <sub>3</sub> +2MPZ | K <sub>2</sub> CO <sub>3</sub> +K-Lys | K <sub>2</sub> CO <sub>3</sub> +K-Sar |
| a <sub>0</sub>                                  | 0.80323                              | 2.65243                               | -0.77631                              |
| a <sub>1</sub>                                  | 0.00716739                           | -2.84098×10 <sup>-3</sup>             | 0.017432                              |
| a <sub>2</sub>                                  | 3.14567×10 <sup>-4</sup>             | -4.05337×10 <sup>-3</sup>             | -0.012271                             |
| a <sub>3</sub>                                  | -3.40862                             | -4.08312                              | -1.56561                              |
| a <sub>4</sub>                                  | 3.88158×10 <sup>-5</sup>             | 4.21053×10 <sup>-5</sup>              | 5.98684×10 <sup>-5</sup>              |
| a <sub>5</sub>                                  | 0.013125                             | 0.01375                               | 4.12500×10 <sup>-3</sup>              |
| a <sub>6</sub>                                  | -0.010329                            | -7.89474×10 <sup>-4</sup>             | 4.40789×10 <sup>-3</sup>              |
| a <sub>7</sub>                                  | -2.71797×10 <sup>-5</sup>            | -1.26750×10 <sup>-5</sup>             | -4.14822×10 <sup>-5</sup>             |
| a <sub>8</sub>                                  | -8.66948×10 <sup>-5</sup>            | -8.02779×10 <sup>-5</sup>             | -5.94702×10 <sup>-5</sup>             |
| a <sub>9</sub>                                  | 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<sub>2</sub>CO<sub>3</sub>+2MPZ solution showed the best performance in terms of CO<sub>2</sub> absorption rate, while K-Sar indicated least effect on absorption rate.

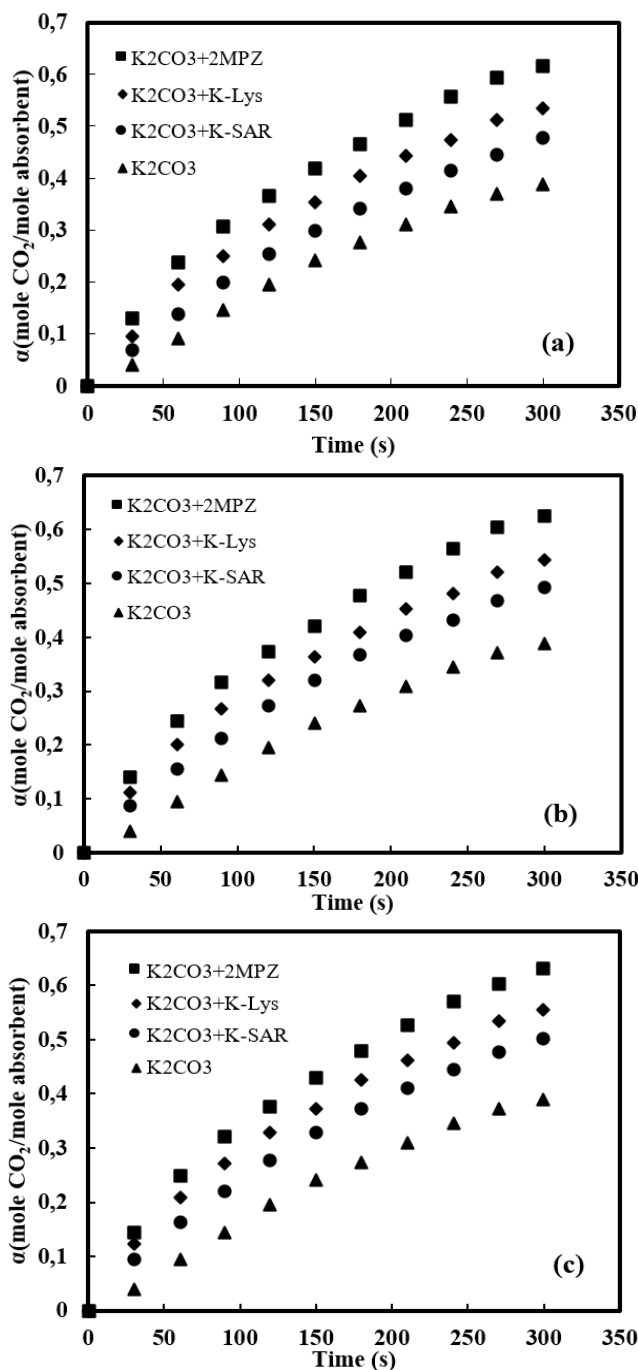


Fig. 5 Comparison of absorption rate in different mole fractions, (a) 0.2, (b) 0.3, (c) 0.4

## 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<sub>2</sub> 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.

- [19] J.H. Song, J.H. Yoon, H. Lee, K. Lee, "Solubility of carbon dioxide in monoethanolamine + ethylene glycol + water and monoethanolamine + poly(ethyleneglycol) + water", *J. Chem. Eng. Data*, vol. 45, pp. 497-499, 1996.
- [20] K. Shen, P. Li, "Solubility of carbon dioxide in aqueous mixtures of monoethanolamine with methyldiethanolamine", *J. Chem. Eng. Data* vol. 37, pp. 96-100, 1992.

#### REFERENCES

- [1] Sh. Ma'mun, H. F. Svendsen, K. A. Hoff, O. Juliussen, "Selection of new absorbents for carbon dioxide capture", *Energy Conversion and Management*, vol. 48, pp. 251-258, 2007.
- [2] P. Chung, A. N. Soriano, R. B. Leron, M. Li, "Equilibrium solubility of carbon dioxide in the amine solvent system of (triethanolamine + piperazine + water)", *J. Chem. Thermodynamics* vol. 42, pp. 802-807, 2010.
- [3] U. E. Aronu, H. F. Svendsen, K. Hoff, "Investigation of amine amino acid salts for carbon dioxide absorption", *International Journal of Greenhouse Gas Control*, vol. 4, pp. 771-775, 2010.
- [4] M. Hamzehic, H. Najibi, "CO<sub>2</sub> solubility in aqueous solutions of potassium proline and (potassium proline and 2-amino-2-methyl-1-propanol) as new absorbents", *Journal of Natural Gas Science and Engineering*, vol. 34, pp. 356-365, 2016.
- [5] A. Haghtalab, E. Ghahremani, "The solubility measurement and modeling of CO<sub>2</sub> in aqueous solution of methyldiethanolamine+2-amino-2-methyl-1-propanol+piperazine at high pressures", *Fluid Phase Equilibria*, vol. 400, pp. 62-75, 2015.
- [6] A. Lee, M. Wolf, N. Kromer, K. A. Mumford, N. Nicholas, S. E. Kentish, G. W. Stevens, "A study of the vapor-liquid equilibrium of CO<sub>2</sub> in mixed solutions of potassium carbonate and potassium glycinate", *International Journal of Greenhouse Gas Control*, vol. 36, pp. 27-33, 2015.
- [7] D. Kang, S. Park, H. Jo, J. Min, J. Park, "Solubility of CO<sub>2</sub> in amino-acid-based solutions of (potassium sarcosinate), (potassium alaninate + piperazine), and (potassium serinate + piperazine)", *J. Chem. Eng. Data*, vol. 58, pp. 1787-1791, 2013.
- [8] Sh. Shen, X. Feng, R. Zhao, U. Ghosh, A. Chen, "Kinetic study of carbon dioxide absorption with aqueous potassium carbonate promoted by arginine", *Chemical Engineering Journal*, vol. 222, pp. 478-487, 2013.
- [9] R. Muraleedharan, A. Mondal, B. Mandal, "Absorption of carbon dioxide into aqueous blends of 2-amino-2-hydroxymethyl-1,3-propanediol and monoethanolamine", *Separation and Purification Technology*, vol. 94, pp. 92-96, 2012.
- [10] S. Mazinani, A. Samsami, A. Jahanmiri, A. Sardarian, "Solubility (at low partial pressures), density, viscosity, and corrosion rate of carbon dioxide in blend solutions of monoethanolamine and sodium glycinate", *J. Chem. Eng. Data*, vol. 56, pp. 3163-3168, 2011.
- [11] H. Balsora, M. Mondal, "Solubility of CO<sub>2</sub> in an aqueous blend of diethanolamine and trisodium phosphate", *J. Chem. Eng. Data*, vol. 56, pp. 4691-4695, 2011.
- [12] Z. Yang, A. Soriano, A. Caparang, M. Li, "Equilibrium solubility of carbon dioxide in (2-amino-2-methyl-1-propanol + piperazine + water)", *J. Chem. Thermodynamics*, vol. 42, pp. 659-665, 2010.
- [13] K. Smith, C. Anderson, "Pro-combustion capture of CO<sub>2</sub> results from solvent absorption pilot, plant trials using 30 wt% potassium carbonate and boric acid promoted potassium carbonate solvent". *Int. J. Greenh Gas. Con.*, vol. 10, pp. 64-73, 2012.
- [14] A. Shrier, P. Danckwerts, "Carbon Dioxide Absorption into Amine-Promoted Potash Solutions", *Ind. Eng. Chem. Fundam.*, vol. 8, pp. 415-423, 1969.
- [15] Y. Kim, J. H. Choi, S. Nam, Y. Yoon, "CO<sub>2</sub> absorption capacity using aqueous potassium carbonate with 2-methylpiperazine and piperazine", *J. Ind. Eng. Chem.* Vol. 18, pp. 105-110, 2012.
- [16] U. Aronu, E. Hessen, T. Warberg, K. Hoff, H. Svendsen, "Vapor-liquid equilibrium in amino acid salt system: Experiments and modeling", *Chemical Engineering Science* vol. 66, pp. 2191-2198, 2011.
- [17] Sh. Shen, Y. Yang, Y. Bian, Y. Zhao, "Kinetics of CO<sub>2</sub> Absorption into aqueous basic amino acid salt: potassium salt of lysine solution", *Environ. Sci. Technol.*, vol. 50, pp 2054-2063, 2016.
- [18] J. Lee, I. Otto, "Equilibrium between carbon dioxide and aqueous monoethanolamine solutions", *J. Appl. Chem. Bio. Techn.*, vol. 26, pp. 541-549, 1976.