CO_2 Solubility in Electrolyte Solution of Potassium Carbonate with the Addition of Promotor Amines (MDEA-DEA/ PZ-DEA) at Various Temperatures

Saidah Altway, Kuswandi Kuswandi*, Iqwal Zulfetra & Firda Nuharani

Department of Chemical Engineering, Faculty of Industrial Technology
Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo,
Surabaya 60111, Indonesia
*E-mail: kuswandi@chem-eng.its.ac.id

Abstract. Carbon dioxide has a huge impact on the increase of greenhouse gas formation causing global warming and climate change. The most effective method to capture CO_2 is chemical absorption using potassium carbonate (K_2CO_3) solution and amines as additive to enhance the absorption rate. CO_2 solubilities in 30% of K_2CO_3 and 5% of the total composition of mixed methyldiethanolamine (MDEA)–diethanolamine (DEA) / piperazine (PZ)-DEA solutions at various temperatures of 303.15-323.15 K and atmospheric pressure are reported. The solubility data were measured using an equilibrium cell apparatus with the N_2O analogy method. The E-NRTL model was used to correlate the experimental data accurately. The binary interaction parameters of the model for the CO_2-K_2CO_3-MDEA-DEA-H_2O and CO_2-K_2CO_3-PZ-DEA-H_2O systems were obtained. The CO_2 physical solubility in 30% of K_2CO_3, 5% of PZ, and 0% of DEA at 303.15 K had the highest value, while the Henry constant of CO_2 in this solution had the lowest value. The CO_2 loading increased with increasing partial pressure of CO_2, while the CO_2 solubility decreased with increasing temperature. Any increase in MDEA concentration from 0% to 5% enhanced the CO_2 partial pressure, otherwise, an increase in PZ concentration from 0% to 5% decreased the CO_2 partial pressure.

Keywords: *amines; binary interaction parameter; CO_2 solubility; E-NRTL model; N_2O analogy.*

1 Introduction

The increase of greenhouse gas in the atmosphere is the main cause of global warming and climate change in the world today. Herein, CO_2 is the most dominant cause. In the industrial sector, CO_2 gas is contained in flue gas produced by industrial equipment. The flue gas is carried to the stack and discharged into the atmosphere, which causes rising CO_2 levels and further causes global warming [1]. Indonesia is in the top 10 of the largest CO_2 emitters in the world, accounting for 2.31% of global CO_2 emissions via the energy sector and deforestation in 2014-2015 [2].

Received May 10th, 2015, 1st Revision April 21st, 2016, 2nd Revision November 28th, 2016, Accepted for publication December 16th, 2016.
 ISSN: 2337-5779, DOI: 10.5614/j.eng.technol.sci.2016.48.6.3

There are several methods that can be used to capture CO_2 from the gas stream. Chemical absorption is a technology that is well developed and has been applied in a variety of commercial processes [3]. Cullinane [4] found that the most effective solvent to capture CO_2 gas is alkanolamine and 'hot' K_2CO_3. Types of amine solvents that have been widely investigated are MEA, DEA, MDEA, TEA, PZ, AMP, and others [5-9].

The most important parameter to determine the equilibrium concentration in the liquid phase and the CO_2 absorption rate is the physical solubility of CO_2 [4,10]. These data are required as a reference for designing absorption columns for industry. Physical solubility of CO_2 in amine solvent cannot be measured directly due to a chemical reaction between CO_2 and amines. CO_2 reacts rapidly with amine so that the physical solubility cannot be determined [4,10]. Therefore, Clarke [11] used the nitrous oxide (N_2O) analogy method to estimate the solubility of CO_2 gas in amine solvent. Carbon dioxide and nitrous oxide have the same molecular structure, molecular interaction parameter, mass, and electron configuration. Therefore, the ratio of the CO_2 and N_2O solubilities (H_{CO2} / H_{N2O}) in organic solvent and water is assumed to be similar at the same temperature.

Several researchers [4,12-14] have indicated that the use of K_2CO_3 as solvent, which blends with amine as promotor, can improve the performance of K_2CO_3 and enhance the absorption rate. The objective of this study was to determine the CO_2 solubility in 30% of K_2CO_3 as solvent and 5% of MDEA-DEA/ PZ-DEA mixtures as promotor at various temperatures between 303.15 and 323.15 K and atmospheric pressure by an equilibrium cell apparatus with the N_2O analogy method. The experimental data were correlated using the E-NRTL model.

2 Experiment

2.1 Materials

MDEA and PZ with purity levels higher than 99% were purchased from Merck, Germany. DEA with purity level higher than 98% was purchased from Sigma-Aldrich, USA. Nitrous oxide with purity level higher than 99% and 20% CO_2-80% N_2 gas mixture were purchased from local company Trigases. Potassium carbonate with 99% purity was purchased from local company Bratachemical. The distilled water used in this study was provided by our laboratory. All materials were used without additional purification.

2.2 Experimental Apparatus and Procedures

The experiment of this study was conducted at 303.15-323.15 K and atmospheric pressure to obtain the solubility of CO_2 in 30% of K_2CO_3 solution and 5% of amine (MDEA-DEA) and (PZ-DEA) mixtures with the N_2O analogy method using an equilibrium cell apparatus. The apparatus used in this study was based on the apparatus used by Haimour and Sandall [10] and Al-Ghawas, *et al*. [15]. It has been described and validated in our previous study [16].

The solubility of N_2O in solution can be obtained from Eq. (1), in which $C^*_{N_2O}$ is the N_2O concentration at equilibrium.

$$H_{N_2O} = \frac{P_{N_2O}}{C^*_{N_2O}} \tag{1}$$

The partial pressure of N_2O is determined from the atmospheric pressure (total pressure measured), which is corrected with the vapor pressure of water [15].

The solubility of CO_2 can be estimated by the N_2O analogy method, as represented in Eq. (2), after the solubility of N_2O has been determined experimentally.

$$H_{CO_2} = H_{N_2O}\left(H^{\circ}_{CO_2} / H^{\circ}_{N_2O}\right) \tag{2}$$

The solubility of CO_2 in water, H^{o}_{CO2}, and the solubility of N_2O in water, H^{o}_{N2O}, are calculated from [17].

The CO_2 partial pressure can be calculated experimentally with Eq. (3) as follows:

$$P^{\exp}_{CO_2} = H_{CO_2} \cdot C^*_{CO_2} \tag{3}$$

in which $C^*_{CO_2}$ is the CO_2 concentration dissolved in the solution at equilibrium. The CO_2 concentration dissolved at equilibrium was determined by passing CO_2 gas into the equilibrium cell apparatus with the same method as in the N_2O experiment. Thus by titration, the concentration of each component in the solution can be obtained.

The E-NRTL model was used to correlate the experimental data. The E-NRTL model contains two contributions. The first one, developed from the local interactions, is determined by the NRTL model [18]. The other one, developed

from the long-range interactions, is calculated by the Pitzer-Debye-Huckel (PDH) model [19]. The activity coefficient (γ) of the E-NRTL model for each component has been described in previous researches [5,16,18]. The deviation of the CO_2 partial pressure calculated by the E-NRTL model from the experimental data can be determined with Eq. (4), as follows:

$$Deviation = \left(\frac{\sum_{i=1}^{M} \left(P_{CO_2}^{cal}(i) - P_{CO_2}^{\exp}(i) \right) \Big/ P_{CO_2}^{\exp}(i)}{M} \right) \times 100\% \quad (4)$$

3 Results and Discussion

The apparatus validation of this study was performed using water as solvent at 303.15-323.15 K. The validation was based on the previous studies by Versteeg and Swaaij [20], Li and Lai [21], and Al-Ghawas, *et al.* [15]. Validation of the apparatus has been done in our previous study [16]. The Henry constant of CO_2 in 30% of K_2CO_3, 5% of PZ, and 0% of DEA at 303.15 K had the lowest value. This indicates that the CO_2 physical solubility in this solution is the greatest of other compositions, as shown in Figures 1 and 2. Furthermore, these figures present the relationship between 1/T and the Henry constant of CO_2. The higher the value of 1/T, the lower the value of the H_{CO2}. This means that an increase in temperature can enhance the value of the H_{CO2}. The higher the value of the H_{CO2}, the more difficult the CO_2 gas is absorbed in the solution. Thus, the physical solubility of CO_2 in the solution will be greater at lower temperature.

After the equilibrium was reached in the equilibrium cell, samples were taken for conducting a composition analysis. The compositions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in the solution were analyzed by titration. The analysis of the HCO_3^- composition in the solution was conducted to determine the amount of CO_2 reacted. The amount of CO_2 absorbed is equal to the amount of CO_2 reacted and dissolved (did not react) in the solution. The reaction that occurs in the solution at equilibrium is shown in Eq. (5).

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2\ KHCO_3 \quad (5)$$

The formation of HCO_3^- in the solution will increase with the addition of promotor amine. The reaction between amine (MDEA) and CO_2 can be represented by Eq. (6),

$$CH_3-N(CH_2-CH_2-OH)(CH_2-CH_2-OH) + CO_2 + H_2O \rightleftharpoons MDEAH^+ + HCO_3^- \quad (6)$$

Thus the amount of CO_2 reacted can be increased.

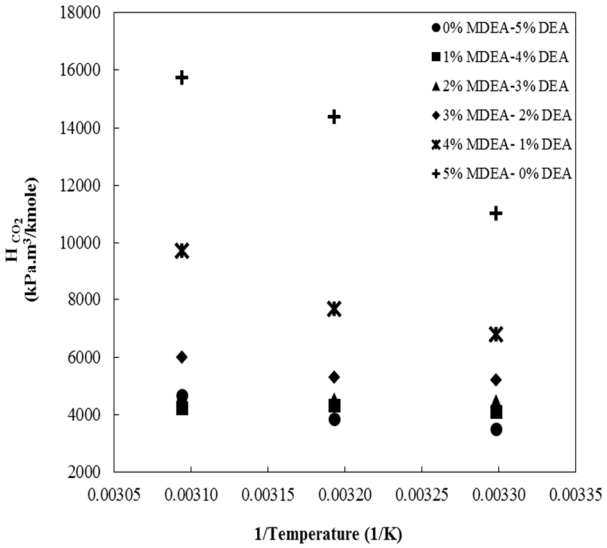

Figure 1 Physical solubility of CO_2 in 30% K_2CO_3, 0-5% MDEA, and 0-5% DEA at 303.15-323.15 K.

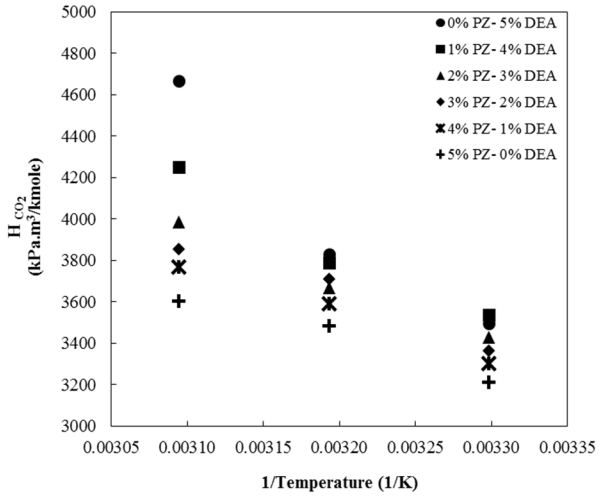

Figure 2 Physical solubility of CO_2 in 30% K_2CO_3, 0-5% PZ, and 0-5% DEA at 303.15-323.15 K.

Figures 3 to 6 show the relationship between temperature and amount of CO_2 reacted and CO_2 dissolved. The reacted CO_2 decreases with temperature increasing from 303.15 to 323.15 K.

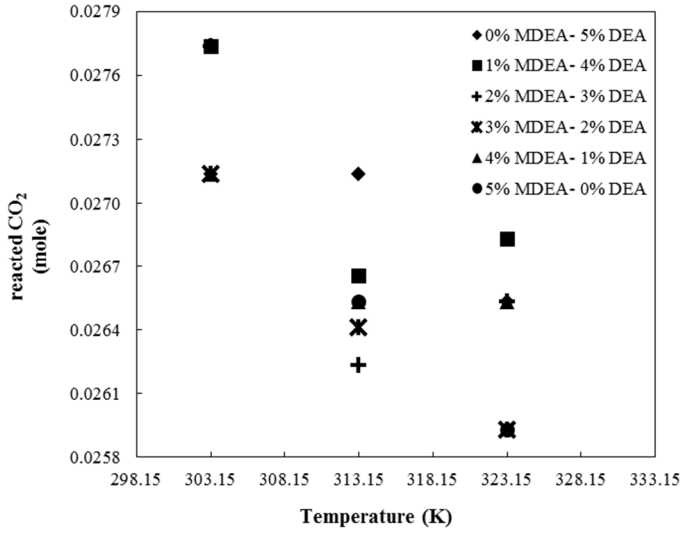

Figure 3 Amount of the CO_2 reacted in 30% K_2CO_3, 0-5% MDEA, and 0-5% DEA at 303.15-323.15 K.

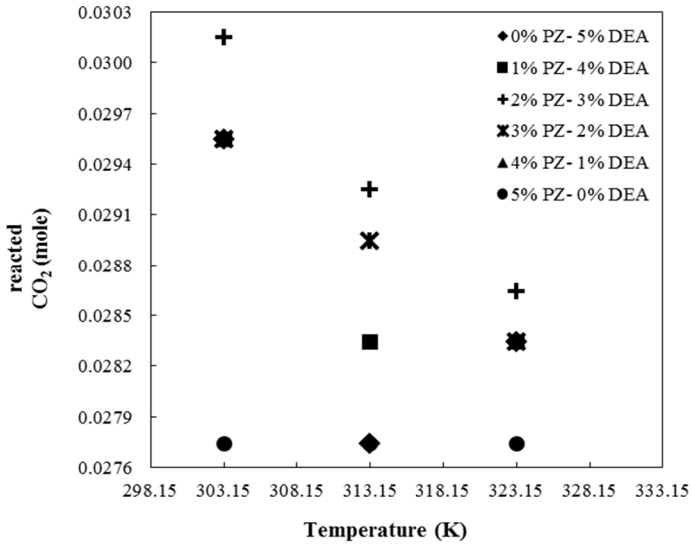

Figure 4 Amount of CO_2 reacted in 30% K_2CO_3, 0-5% PZ, and 0-5% DEA at 303.15-323.15 K.

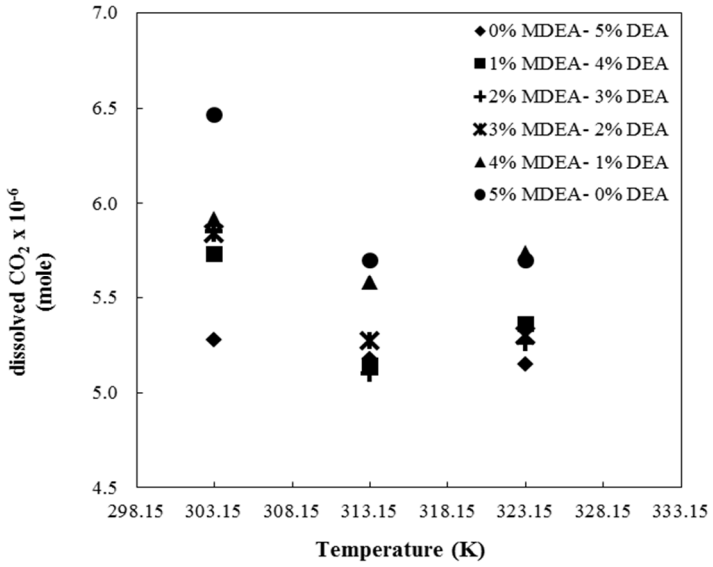

Figure 5 Amount of CO_2 dissolved in 30% K_2CO_3, 0-5% MDEA, and 0-5% DEA at 303.15-323.15 K.

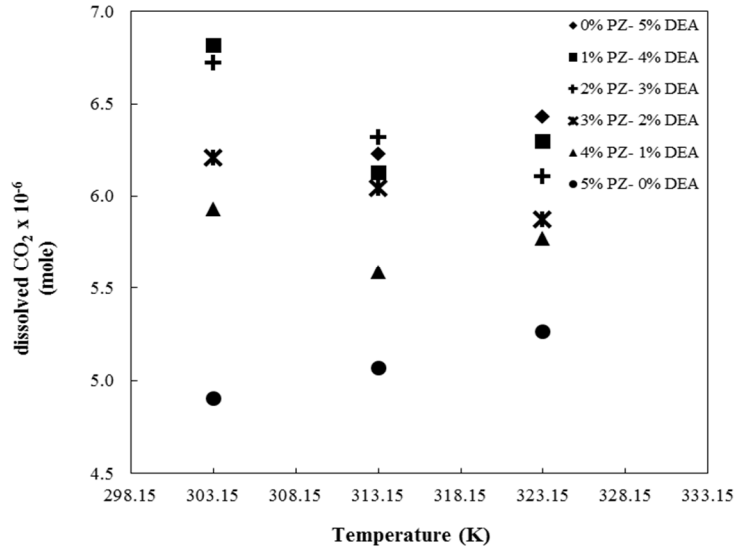

Figure 6 Amount of CO_2 dissolved in 30% K_2CO_3, 0-5% PZ, and 0-5% DEA at 303.15-323.15 K.

The increase in temperature can either increase or reduce the absorption rate of CO_2, depending on which factors are decisive. In this case, the solubility is the

more dominant factor. The CO_2 solubility decreases with increasing temperature. Consequently, the increase in temperature decreases the absorption rate of CO_2. Furthermore, it decreases the amount of CO_2 absorbed, thus the amount of dissolved CO_2 and reacted CO_2 also decreases. It can also be seen that the amount of the reacted CO_2 in the K_2CO_3-PZ-DEA-H_2O solution is greater than that in the K_2CO_3-MDEA-DEA-H_2O solution. This indicates that the PZ-DEA mixture has the ability to react with CO_2 faster and to a higher degree than the MDEA-DEA mixture. The equilibrium constant (K) used by Austgen and Rocelle [22] was applied in this study to calculate the amount of dissolved CO_2.

Based on Figures 7 and 8, the E-NRTL model can correlate well the experimental data for the CO_2-K_2CO_3-MDEA-DEA-H_2O and CO_2-K_2CO_3-PZ-DEA-H_2O systems with a deviation of 8.82% and 2.53% respectively. This shows that an increase in CO_2 partial pressure increases CO_2 loading. The CO_2 loading can be determined from the ratio of the total amount of absorbed CO_2 to the amount of K+ and amines in the solution. The greater the CO_2 loading, the greater the amount of absorbed CO_2.

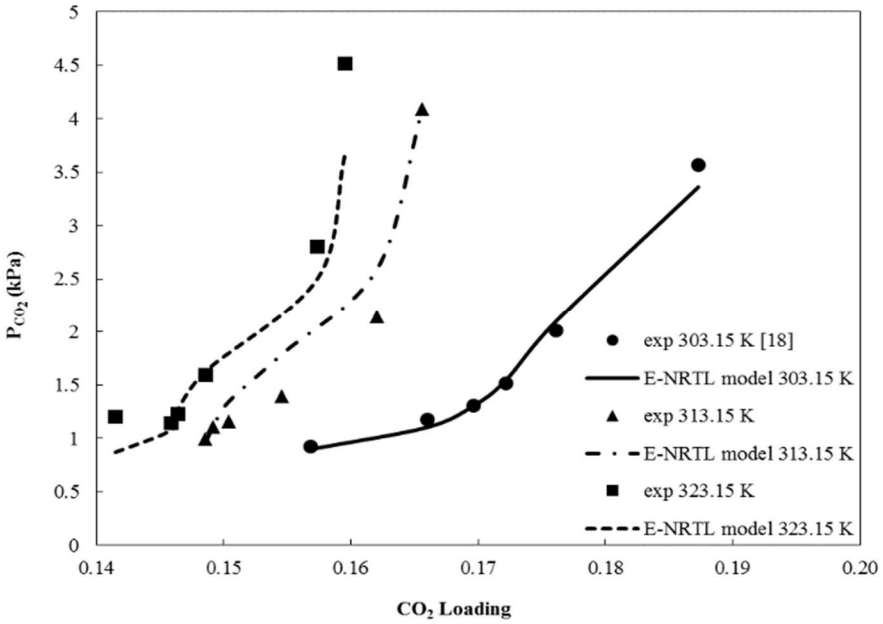

Figure 7 Comparison of calculated CO_2 partial pressure by E-NRTL model with experimental data of CO_2-K_2CO_3-(MDEA+DEA)-H_2O system at 303.15-323.15 K.

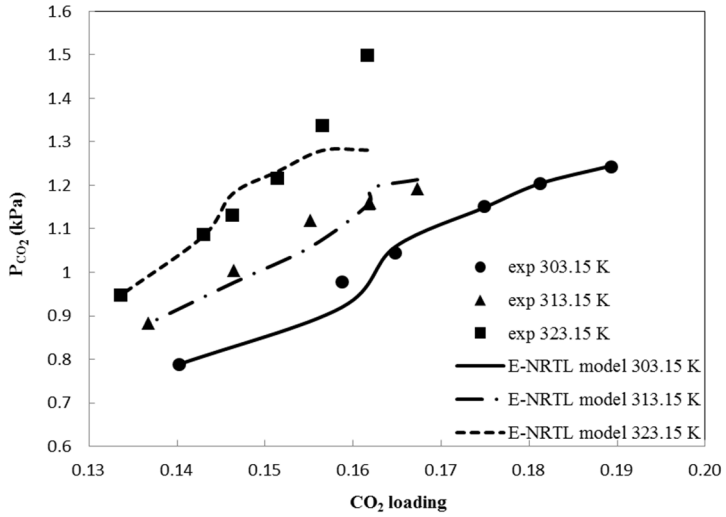

Figure 8 Comparison of calculated CO_2 partial pressure by E-NRTL model with experimental data of CO_2-K_2CO_3-(PZ+DEA)-H_2O system at 303.15-323.15 K.

Furthermore, it can also be seen that the mixture of MDEA-DEA as promotor enhances the partial pressure of CO_2 from 0.9 to 4.5 kPa, while the CO_2 loading ranged from 0.14 to 0.19 for any increase of MDEA concentration from 0% to 5%. On the other hand, an increase of PZ concentration decreases the CO_2 partial pressure. From 5% to 0% of PZ, the CO_2 partial pressure ranged from 0.7 to 1.5 kPa and the CO_2 loading ranged from 0.13 to 0.19 at 303.15-323.15 K.

At the same temperature and composition of the MDEA-DEA and PZ-DEA mixtures, the solubility of CO_2 in K_2CO_3-PZ-DEA-H_2O solution was higher than that in K_2CO_3-MDEA-DEA-H_2O solution. This can be seen from the Henry constant value and the CO_2 partial pressure in the CO_2-K_2CO_3-PZ-DEA-H_2O system, which are lower than that in the CO_2-K_2CO_3-MDEA-DEA-H_2O system. The partial pressure of CO_2 is at equilibrium with the composition of CO_2 dissolved in the solution. The lower the CO_2 partial pressure, the lower the amount of CO_2 dissolved. Thus, the PZ-DEA promotor is able to react with CO_2 to a higher degree than the MDEA-DEA promotor.

There are interactions between molecule-ions (cation, anion), ion-molecule, and molecule-molecule in the electrolyte solution. As shown in Tables 1 and 2, the binary interaction parameters of the E-NRTL model were obtained in this study by fitting the experimental data and by minimizing the deviation between the calculated and the experimental CO_2 partial pressures as listed in Eq. (4).

Table 1 Binary interaction parameters of the E-NRTL model for CO_2-K_2CO_3-MDEA-DEA-H_2O system.

Interaction Pair	A	B
H_2O-K^+,CO_3^{2-}	0.2906	1581.9477
K^+,CO_3^{2-}-H_2O	16.8260	-376.9776
H_2O-K^+,HCO_3^-	3.5466	2862.9717
K^+,HCO_3^--H_2O	1.6992	-601.0102
CO_2-K^+,CO_3^{2-}	18.1601	0.0190
K^+,CO_3^{2-}-CO_2	-3.6034	0.0020
CO_2-K^+,HCO_3^-	13.7406	0.0050
K^+,HCO_3^--CO_2	-7.5882	0.0116
MDEA-K^+,CO_3^{2-}	15.9018	-0.0022
K^+,CO_3^{2-}—MDEA	-16.6288	0.0080
MDEA-K^+,HCO_3^-	13.4431	0.0312
K^+,HCO_3^-—MDEA	-9.9209	-0.0119
DEA-K^+,CO_3^{2-}	14.2215	0.0017
K^+,CO_3^{2-}—DEA	-49.7068	-0.0265
DEA-K^+,HCO_3^-	18.1363	0.00003
K^+,HCO_3^-—DEA	-32.0727	0.0032
CO_2-H_2O	27.6063	-8428.9780
H_2O-CO_2	-3.9847	1080.0234
H_2O-MDEA	38.5937	-1547.9046
MDEA-H_2O	8.4030	-1029.9708
MDEA-CO_2	6.9470	0.0222
CO_2-MDEA	-0.0013	0.0003
H_2O-DEA	110.9578	1317.9671
DEA-H_2O	8.2146	-718.0496
DEA-CO_2	-4.0545	-0.0053
CO_2-DEA	19.0643	0.0992
DEA-MDEA	4.3455	0.0154
MDEA-DEA	15.7693	0.0505

Table 2 Binary interaction parameters of the E-NRTL model for CO_2-K_2CO_3-PZ-DEA-H_2O system.

Interaction Pair	A	B
H_2O-K^+,CO_3^{2-}	6.5868	1582.0180
K^+,CO_3^{2-}-H_2O	22.0015	-376.9981
H_2O-K^+,HCO_3^-	13.4615	2862.9924
K^+,HCO_3^--H_2O	-2.3622	-600.9386
CO_2-K^+,CO_3^{2-}	11.9452	-0.0003
K^+,CO_3^{2-}-CO_2	6.9734	0.0043
CO_2-K^+,HCO_3^-	12.4738	-0.0118
K^+,HCO_3^--CO_2	18.0367	0.0053
PZ-K^+,CO_3^{2-}	21.8881	0.0056
K^+,CO_3^{2-}—PZ	-1.9255	-0.0031
PZ-K^+,HCO_3^-	15.9018	0.0148
K^+,HCO_3^-—PZ	-6.9958	0.0035
DEA-K^+,CO_3^{2-}	12.1837	-0.0010
K^+,CO_3^{2-}—DEA	-9.3069	-0.0008
DEA-K^+,HCO_3^-	13.9665	0.0038
K^+,HCO_3^-—DEA	-3.4174	0.0007
CO_2-H_2O	31.7369	-8428.9770
H_2O-CO_2	-2.3121	1080.0703
H_2O-PZ	-8.0646	-0.0233
PZ-H_2O	-1.3528	-0.0209
PZ-CO_2	4.7064	0.0182
CO_2-PZ	-0.0003	0.0003
H_2O-DEA	-6.5097	1317.6078
DEA-H_2O	1.4480	-718.0867
DEA-CO_2	-3.4001	-0.0127
CO_2-DEA	3.5859	0.0116
DEA-PZ	-0.3741	-0.0009
PZ-DEA	-2.5949	-0.0080

4 Conclusions

The physical solubility of CO_2 in K_2CO_3 solution with a mixture of amines had the greatest value in the composition of 30% K_2CO_3, 5% PZ and 0% DEA at 303.15 K, while the Henry constant of CO_2 in this solution had the lowest value. An increase in CO_2 partial pressure increased the value of CO_2 loading. The solubility of CO_2 decreased with an increase in temperature. In a mixed solution of K_2CO_3 with MDEA-DEA promotor, any increase in MDEA concentration from 0% to 5% increased the partial pressure of CO_2 from 0.9 to 4.5 kPa, while the CO_2 loading ranged from 0.14 to 0.19. Otherwise, the CO_2 partial pressure decreased with an increase in PZ concentration. From 5% to 0% of PZ concentration, the CO_2 partial pressure ranged from 0.7 to 1.5 kPa and the CO_2 loading ranged from 0.13 to 0.19 at 303.15-323.15 K. The E-NRTL model can correlate well the experimental data. The binary interaction parameters of the E-NRTL model were also obtained in this study.

Acknowledgements

The authors are grateful for the financial support provided by PNBP ITS, through grant no. 038839.28/IT2.11/PN.01.00/2014.

References

[1] Figueroa, J.D., Fout, T., Plasynski, S., McIlvried, H. & Srivastava, R.D., *Advances in CO_2 Capture Technology-The U.S. Department of Energy's Carbon Sequestration Program*, Int. Journal of Greenhouse Gas Control, **2**, pp. 9-20, 2008.

[2] Burck, J., Marten, F. & Bals, C., *The Climate Change Performance Index Results 2015*, Germanwatch & Climate Action Network, Bonn, Germany, Europe, 2014.

[3] Rao, A.B. & Rubin, E.S., *A Technical, Economic, and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control*, Environ. Sci. Tech., **36**(20), pp. 4467-4475, 2002.

[4] Cullinane, J.T., *Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption*, Dissertation, University of Texas, Austin, United States, 2005.

[5] Austgen, D.M., Rochelle, G.T., Peng, X. & Chen, C.C., *Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems using the Electrolyte-NRTL Equation*, Ind. Eng. Chem. Res., **28**(7), pp. 1060-1073, 1989.

[6] Liu, Y., Zhang, L. & Watanasiri, S., *Representing Vapor-Liquid Equilibrium for an Aqueous MEA- CO_2*, Ind. Eng. Chem. Res., **38**(5), pp. 2080-2090, 1999.

[7] Park, H.S., Lee, K.B., Hyun, J.C. & Kim, S.H., *Correlation and Prediction of the Solubility of Carbon Dioxide in Aqueous Alkanolamine and Mixed Alkanolamine Solutions*, Ind. Eng. Chem. Res., **41**(6), 1658-1665, 2002.

[8] Chung, P-Y., Soriano, A.N., Leron, R.B. & Li, M-H., *Equilibrium Solubility of Carbondioxide in the Amine Solvent System of (Triethanolamine+Piperazine+Water)*, J. Chem. Thermodynamics, **42**(6), pp. 802-807, 2010.

[9] Kamalpour, S. & Mehablia, A., *Thermodynamics of CO_2-MDEA using eNRTL with Differential Evolution Algorithm*, International Journal of Thermodynamics, **15**(3), pp. 157-168, 2012.

[10] Haimour, N. & Sandall, O.C., *Absorption of Carbon Dioxide into Aqueous Methyldiethanolamine*, Chem. Eng. Science, **39**(12), pp. 1791-1796, 1984.

[11] Clarke, J.K.A., *Kinetics of Absorption of Carbon Dioxide In Monoethanolamine Solutions at Short Contact Times*, Ind. Eng. Chem. Fundamental, **3**(3), pp. 239-245, 1964.

[12] Savage, D.W., Sartori, G. & Astarita, G., *Amines as Rate Promotors for Carbon Dioxide Hydrolysis, Faraday Discuss*, Chem. Soc., **77**, pp.17-31, 1984.

[13] Cullinane, J.T. & Rochelle, G.T., *Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine*, Chem.Eng. Sci., **59**(17), pp.3619-3630, 2004.

[14] Rahimpour, M.R. & Kashkooli, A.Z., *Enhanced Carbon Dioxide Removal by Promoted Hot Potassium Carbonate in a Split-Flow Absorber*, Chem. Eng. Proc., **43**(7), pp. 857-865, 2004.

[15] Al-Ghawas, H.A., Hagewiesche, D.P., Ruiz-Ibanez, G. & Sandall, O.C., *Physicochemical Properties Important for Carbon Dioxide Absorption in Aqueous Methyldiethanolamine*, J. Chem. Eng. Data, **34**(4), pp. 385-391, 1989.

[16] Altway, S., Kuswandi, Zulfetra, I. & Nuharani, F., *Experiment and Correlation of CO_2 Solubility in Electrolyte Solution of K_2CO_3-(MDEA+DEA)-H_2O*, Proceeding of International Seminar Chemical Engineering in Minerals and Materials Processing in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo, Bandung, Indonesia, 2014.

[17] Tourneux, D.L., Iliuta, I., Iliuta, M.C., Fradette, S. & Larachi, F., *Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-Hydroxymethyl-1,3-Propanediol*, Fluid Phase Equilib., **268**, pp. 121-129, 2008.

[18] Chen, C.C., *A Segment-Based Local Composition Model for the Gibbs Energy of Polymer Solutions*, Fluid Phase Equilib., **83**, pp. 301-312, 1993.

[19] Pitzer, K.S., *Electrolytes: From Dilute Solutions to Fused Salts*, J.Am.Chem.Soc., **102**(9), pp. 2902-2906, 1980.

[20] Versteeg, G.F. & van Swaaij, W.P.M., *Solubility and Diffusivity of Acid Gases (CO_2, N_2O) in Aqueous Alkanolamine Solutions*, J. Chem. Eng. Data, **33**(1), pp. 29-34, 1988.

[21] Li, M.H. & Lai, M.D., *Solubility and Diffusivity of N_2O and CO_2 in (Monoethanolamine +N-Methyldiethanolamine + Water) and in (Monoethanolamine +2-Amino-2-methyl-1-propanol + Water*), J. Chem. Eng. Data, **40**(2), pp. 486-492, 1995.

[22] Austgen, D.M., Rochelle, G.T. & Chen, C.C., *Model of Vapor Liquid Equilibria for Aqueous Acid Gas-alkanolamine Systems. 2. Representation of H_2S and CO_2 Solubility in Aqueous MDEA and CO_2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA*, Ind. Eng. Chem. Res., **30**(3), pp. 543-555, 1991.