Prediction of Gas-Liquid Equilibria of CO_2-K_2CO_3-MDEA-H_2O System by Electrolyte UNIQUAC Model

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Abstract —Carbon dioxide is an acid gas that can be harmful impurity especially in the chemical industry. Various processes have been developed to reduce the CO_2 from the gas stream. Chemical absorption is the most economical method for CO_2 separation. One of the processes that is widely used in industries is Benfield process with K_2CO_3 (potassium carbonate) as a solvent and amine as a promotor. In this study, MDEA (Methyldiethanolamine) is used as a promotor. As a reference for designing CO_2 absorption/stripping packed column in industries, gas-liquid equilibrium data were required. The objective of this study is to predict the gas-liquid equilibria of CO_2-K_2CO_3-MDEA-H_2O system at 30^oC and atmospheric pressure with 30% K_2CO_3 and variation of weight percent of MDEA 2, 5, 8, and 10%. The model used in this study is an electrolyte UNIQUAC. The simulation was conducted using Matlab programming. The deviation of predicted CO_2 partial pressure with the experimental data is 14.85%. The energy interaction parameters of electrolyte UNIQUAC model were obtained from fitting with the experimental data by Least Square method. The results of this study represented that with increasing CO_2 partial pressure, CO_2 loading increased, and also at the same partial pressure of CO_2, CO_2 loading increased with the increase of weight percent of MDEA

I. INTRODUCTION

Carbon dioxide (CO_2) has to be removed from the gas stream, since CO_2 induces several losses in industries. CO_2 is an acid gas which is corrosive and it causes damage the plant utility and the piping system. In the natural gas liquefaction process, CO_2 can freeze at very low temperature and block the piping system. Besides, it will cause damage the tube in the heat exchanger. In the turbine CO_2 gas will reduce the heating value of combustion. In the ammonia synthesis unit, CO_2 is a poison to the catalyst. Hence it is necessary to reduce CO_2 from the gas stream. Various processes can be used for CO_2 separation. Rao and Rubin [1] represented that there are several technology in CO_2 capture, such as cryogenic, membrane, adsorption, and the most economical method for CO_2 separation is chemical absorption.

Dang and Rochelle [2] indicated that energy consumption for solvent regeneration is the biggest cost factor for CO_2 capture, which can reach 49% of the total cost of CO_2 capture. Furthermore, another factor is the solvent capacity which can specify the total amount of CO_2 absorbed per unit of solvent. Wide variety of solvents can be used in the gas processing to separate CO_2 gas, however Cullinane [3] showed that pottasium carbonate and alkanolamine are the most effective solvents.

Many researchers have studied the predictive model for various solvents in carbon dioxide removal. Sander et al. [4] studied the calculation of gas-liquid equilibria in mixed solvent/salt systems by an extended UNIQUAC model. Austgen et al. [5] conducted the modeling of gas-liquid equilibria for acid gas-alkanolamine aqueous solution system by the electrolyte-NRTL model. Posey [6] investigated thermodynamics model for acid gas in alkanolamine aqueous solutions.

Hilliard [7] predicted the model of potassium carbonate/piperazine/ethanolamine aqueous solution for carbon dioxide removal from flue gas. Benamor and Aroua [8] conducted the modeling of CO_2 solubility and carbamate concentration in DEA, MDEA and their mixtures by the Deshmukh-Mather model. Haider et al. [9] studied equilibrium solubility of carbon dioxide in 2(methylamino)ethanol by Kent–Eisenberg model. Kamalpour and Mehablia [10] investigated thermodynamics model of CO_2-MDEA using E-NRTL with differential evolution algorithm.

Potassium carbonate (K_2CO_3) has a low heat regeneration, low cost, and high stability, but it has low reaction rate [11, 12]. Whereas, alkanolamine has a low cost and high reaction rate. However there are several drawbacks of alkanolamine such as it has a high vapor pressure and high heat absorption (20-25 kcal/mol). Moreover, it cannot remove the mercaptan compounds and at temperature above 100^oC it can be degraded. In primary amine (Monoethanolamine and Diglycolamine) and secondary amine (Diethanolamine and Diisopropanolamine), it can establish a stable carbamate compounds. In addition, byproducts that cannot be degraded can present in the further reaction [13]. Thus, to

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improve the overall performance of solvents and increase the absorption rate of CO_2, it can be used Benfield process, which uses alkanolamine as a promotor in K_2CO_3 aqueous solution [3, 14, 15, 16].
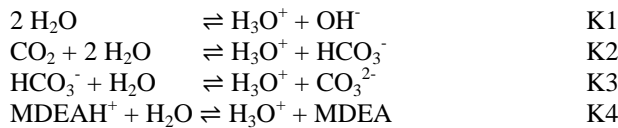
Potassium carbonate as a solvent and MDEA as a promotor were used in the present study. The advantages of MDEA as a tertiary amine group compared to other alkanolamine are lower heat regeneration, lower vapor pressure, higher corrosion resistance, higher acid gas loading, higher degradation resistance, higher fouling resistance and foaming resistance [17]. The objective of this study is to predict the gas-liquid equilibria of CO_2-K_2CO_3-MDEA-H_2O system at 30^oC and atmospheric pressure with 30% K_2CO_3 and variation of MDEA weight percent 2, 5, 8, and 10% by electrolyte UNIQUAC model. The simulation was conducted using Matlab programming. The energy interaction parameters of electrolyte UNIQUAC model were obtained using Least Square method.

II. METHOD

A. Calculation of Lift Coefficient

This study intended to predict the gas-liquid equilibria of CO_2-K_2CO_3-MDEA-H_2O system at 30^oC and atmospheric pressure with 30% K_2CO_3 and variation of weight percent of MDEA 2, 5, 8, and 10% by electrolyte UNIQUAC model. The influent gas was a mix gas of CO_2-N_2 with N_2 as an inert. The composition of mix gas was 10-20% CO_2 and 80-90% N_2. The simulation was conducted using Matlab version 6. The energy interaction parameters of electrolyte UNIQUAC model were obtained by fitting with the experimental data [18] using Least Square method.

The reaction for CO_2-K_2CO_3-MDEA-H_2O system are as follows :

$2 H_2O$	$\rightleftharpoons H_3O^+ + OH^-$	K1
$CO_2 + 2 H_2O$	$\rightleftharpoons H_3O^+ + HCO_3^-$	K2
$HCO_3^- + H_2O$	$\rightleftharpoons H_3O^+ + CO_3^{2-}$	K3
$MDEAH^+ + H_2O$	$\rightleftharpoons H_3O^+ + MDEA$	K4

Components calculated in this study are H_2O, CO_2, MDEA, K^+, CO_3^{2-}, and HCO_3^-. While H_3O^+, OH^-, and $MDEAH^+$ are ignored because the value are very small. From the reaction above, the element balances as follows:

$$2x_{H_2O} + x_{HCO_3^-} - \frac{n_{Htot}}{n_{tot}} = 0 \tag{1}$$

$$x_{CO_2} + x_{CO_3^{2-}} + x_{HCO_3^-} - \frac{n_{Ctot}}{n_{tot}} = 0 \tag{2}$$

$$x_{H_2O} + 2x_{CO_2} + 3x_{CO_3^{2-}} + 3x_{HCO_3^-} - \frac{n_{Otot}}{n_{tot}} = 0 \tag{3}$$

$$x_{MDEA} - \frac{n_{MDEAtot}}{n_{tot}} = 0 \tag{4}$$

$$x_{K^+} - \frac{n_{Ktot}}{n_{tot}} = 0 \tag{5}$$

The lagrange multiplier (λ_k) is used for each element, thus the chemical potential for each component is as follows:

$$\mu_{H_2O} - 2\psi_H - \psi_O = 0 \tag{6}$$

$$\mu_{CO_2} - \psi_C - 2\psi_O = 0 \tag{7}$$

$$\mu_{HCO_3^-} - 2\psi_H - \psi_O = 0 \tag{8}$$

$$\mu_{MDEA} - \psi_{MDEA} = 0 \tag{9}$$

$$\mu_{CO_3^{2-}} - \psi_C - 3\psi_O = 0 \tag{10}$$

$$\mu_{K^+} - \psi_K = 0 \tag{11}$$

$$x_{H_2O} + x_{CO_2} + x_{CO_3^{2-}} + x_{HCO_3^-} + x_{K^+} + x_{MDEA} - 1 = 0 \tag{12}$$

Where,

$$\psi_k = \frac{\lambda_k}{RT}$$

$$n_{tot} = n_{H_2O} + n_{CO_2} + n_{CO_3^{2-}} + n_{HCO_3^-} + n_{K^+} + n_{MDEA}$$

$x_i = n_i/(n_{tot})$

$i = H_2O, CO_2, MDEA, CO_3^{2-}, HCO_3^-, K^+$

The chemical potential for non-ideal solution is formulated as:

$$\mu_i = \frac{\mu_i^o}{RT} + \ln x_i + \ln \gamma_i \tag{13}$$

Activity coefficient, γi, is the correction of chemical potential for ideal solution, as the effect of non-ideal solution characteristics.

The equilibrium constant of each reaction is calculated as seen in Equation (14) :

$$\ln K = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T \tag{14}$$

Thus the standard chemical potential μ_i^o can be calculated from the equilibrium constant K :

$$RT \ln K_j = -\sum_{i=1}^{N} v_{ij} \mu_i^o \qquad j=1,2,...,R \tag{15}$$

Equation (15) shows the system of R equations with N unknown variables. Because N is greater than R, then μ_i^o which are consistent with K in reaction j have the value, while the results of the vector of N minus R from μ_i^o are zero. Equation (15) is solved by Gauss elimination method so that the value of the standard chemical potential μ_i^o can be obtained.

From Equation (1) – Equation (12), there are 12 equations with 12 unknown variables such as $x_{H_2O}, x_{CO_2}, x_{HCO_3^-}, x_{MDEA}, x_{CO_3^{2-}}, x_{K^+}, \psi_H, \psi_C, \psi_O, \psi_K, \psi_{MDEA}$ and the total moles in the liquid phase, n_{tot}.

The simultaneous equations above are calculated by Newton Raphson method and the activity coefficients γ_i are calculated using electrolyte UNIQUAC model, with the initial setting $\gamma_i = 1$, till the values of x_i and γ_i are convergent.

The approach used in electrolyte UNIQUAC model is to assume that the Gibbs energy of electrolyte systems can be considered as the sum of two forms, the first is connected to the long range forces between the ions and the other at short range forces between all species. Debye-Huckel equation is used to represent the contribution of long range ion-ion interactions, which are substantial at low concentration. UNIQUAC equation is used to calculate the contribution of all types of short-range interactions, which are substantial at higher concentration. The advantage of UNIQUAC model is considering size and shape of the molecules through the structural parameters [4], which first used modified UNIQUAC model for electrolyte systems. It is assumed that the short range interactions between pairs of ions and the surface area fraction are randomly

distributed relative to the individual ion, which produce interaction parameter of ion-pair specific. The activity coefficient of various components in the electrolyte system for short range and long range contribution is calculated as follows [19].

For solvent n :

$$\ln \gamma_n = \ln \gamma_n^{dh} + \ln \gamma_n^{C} + \ln \gamma_n^{R} \tag{16}$$

For molecular solute m :

$$\ln \gamma^*_m = \ln \gamma_m^{dh} + \ln \gamma_m^{*,C} + \ln \gamma_m^{*,R} \tag{17}$$

For ionic component i :

$$\ln \gamma^*_i = \ln \gamma_i^{*,dh} + \ln \gamma_i^{*,C} + \ln \gamma_i^{*,R} \tag{18}$$

γ_n^{dh}, $\ln \gamma_m^{dh}$, $\ln \gamma_i^{*,dh}$ can be calculated in Equation (19) – Equation (21).

$$\ln \gamma_n^{dh} = \frac{2AM_n d_s}{b^3 d_n}\left[1 + b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln 1 + b\sqrt{I}\right] \tag{19}$$

$$\ln \gamma_n^{dh} = \frac{2A\bar{v}_{m,w}^{\infty} d_s}{b^3}\left[1 + b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln 1 + b\sqrt{I}\right] \tag{20}$$

Where :

$$A = 1{,}327757 x 10^5 \frac{d_s^{1/2}}{(\varepsilon T)^{3/2}}$$

$$b = 6{,}359696 x 10^5 \frac{d_s^{1/2}}{(\varepsilon T)^{1/2}}$$

$$I_x = \frac{1}{2}\sum_{i=1}^{N_{ion}} x_i z_i^2 \qquad I_k = \frac{I_x}{\sum_{k=1}^{N_{mol}} x_k M_k}$$

$$d_s = \frac{\sum_{k=1}^{N_{mol}} x'_k M_k}{\sum_{k=1}^{N_{mol}}\frac{x'_k M_k}{d_k}} \qquad x'_k = \frac{x_k}{1-\sum_{i=1}^{N_{ion}} x_i}$$

$$\ln \gamma_i^{*,dh} = \frac{A z_i^2 \sqrt{I}}{1+b\sqrt{I}} \tag{21}$$

For γ_n^{C} and γ_n^{R} :

$$\ln \gamma_n^C = \ln\frac{\Phi_n}{x_n} + 1\frac{\Phi_n}{x_n} - \frac{z}{2}q_n\left[\ln\frac{\Phi_n}{\theta_n} - \frac{\Phi_n}{\theta_n} + 1\right] \tag{22}$$

$$\ln \gamma_n^R - q_n[1 - \ln S_n - A_n] \tag{23}$$

While $\gamma_m^{*,C}$, $\gamma_m^{*,R}$, $\gamma_i^{*,C}$, and $\gamma_i^{*,R}$ are calculated as follows:

$$\ln \gamma_l^{*,C} = \ln\frac{\Phi_l}{x_l} - \frac{\Phi_l}{x_l} - \ln\frac{r_l}{r_w} + \frac{r_l}{r_w} - \frac{z}{2}q_l\left[\ln\frac{\Phi_l}{\theta_l} - \frac{\Phi_l}{\theta_l} - \ln\frac{r_l q_w}{r_w q_l} + \frac{r_l q_w}{r_w q_l}\right] \tag{24}$$

$$\ln \gamma_l^{*,R} = q_l[-\ln S_l - A_l + \ln \Psi_{wl} + \Psi_{wl}] \tag{25}$$

$$l = m,i$$

Where :

$$S_l = \sum_k \theta_k \Psi_{kl} \qquad A_l = \sum_k \frac{\theta_k \psi_{lk}}{S_k}$$

$$\psi_{kl} = \exp\left(-\frac{\tau_{kl}}{T}\right) \qquad \theta_l = \frac{q_l x_l}{\sum_k q_k x_k}$$

$$\phi_l = \frac{r_l x_l}{\sum_k r_k x_k} \qquad\qquad k,l = n,m,i$$

In the form of ion pairs, it is assumed that the anion will be randomly distributed among cations and its reverse. The following equation is the surface area fraction of the ion pair [20].

$$\theta_{z_a c,z_c a} = \theta_a \frac{z_c x_c}{\sum_{\acute{c}} z_{\acute{c}} x_{\acute{c}}} + \frac{z_a x_a}{\sum_{\acute{a}} z_{\acute{a}} x_{\acute{a}}} \tag{26}$$

Where $\sum \acute{c}$ and $\sum \acute{a}$ are the average sum of all cations and anions.

The surface area parameter of the ion pair, $q_{z_a c,z_c a}$, can be calculated by Equation (27) :

$$q_{z_a c,z_c a} = z_a q_c + z_a q_c \tag{27}$$

The residual activity coefficient of ions are related to the residual activity coefficient of ion pairs which are appropriate as follows :

$$\ln \gamma^{*,R}_{z_a c,z_c a} = \frac{z_a}{z_a + z_c}\ln \gamma_c^{*,R} + \frac{z_c}{z_a + z_c}\ln \gamma_a^{*,R} \tag{28}$$

To solve Equation (28), it can be assumed for each ion pair $\gamma_c^{*,R}$ is equal $\gamma_a^{*,R}$ to as given in Equation (29).

$$\ln \gamma^{*,R}_{z_a c,z_c a} = \ln \gamma_c^{*,R} = \ln \gamma_a^{*,R} \tag{29}$$

Equation (29) represents the relationship between activity coefficient of ion pair and individual ion. The combination of them is to obtain the ionic activity coefficient, as shown from the following equation :

$$\langle\ln \gamma_c^{*,R}\rangle = \sum_a \left[\frac{\theta_{z_a c,z_c a}}{\sum_{a'}\theta_{z_{a'} c,z_c a'}}\right]\ln\left(\gamma_c^{*,R}\right)_a \tag{30}$$

$$\langle\ln \gamma_a^{*,R}\rangle = \sum_c \left[\frac{\theta_{z_a c,z_c a}}{\sum_{\acute{c}}\theta_{z_a c',z_{c'} a}}\right]\ln\left(\gamma_a^{*,R}\right)_c \tag{31}$$

After the composition in the liquid phase x_i and the activity coefficient γ_i have been obtained, the partial pressure and the composition of CO_2 in the gas phase can be calculated from the following equation :

$$P_{CO_2} = x_{CO_2} H_{CO_2} \tag{32}$$

$$y_{CO_2} = \frac{P_{CO_2}}{P_{tot}} \tag{33}$$

H_{CO_2} is the Henry constant of CO_2 in the solution associated with $H_{CO_2}^w$, Henry constant of CO_2 in pure water through the activity coefficient γ_i :

$$H_{CO_2} = \gamma_{CO_2} H_{CO_2}^w \tag{34}$$

Henry constant of CO_2 in pure water is determined from the following correlation equation [21] :

$$\ln H_{CO_2}^w = 170.7126 - \frac{8477.771}{T} - 21.95743\ln T + 0.005781T \tag{35}$$

Whereas the partial pressure and the composition of H_2O in the gas phase can be calculated by the Equation (36) and (37) as follows :

$$P_{H_2O} = x_{H_2O}\gamma_{H_2O} P_{H_2O}^S \tag{36}$$

$$y_{H_2O} = \frac{P_{H_2O}}{P_{tot}} \tag{37}$$

$P_{H_2O}^S$ is the saturated pressure of H_2O and P_{tot} is the total pressure.

The deviation of calculated and experimental CO_2 partial pressure was calculated as follows :

$$Error = \left[\frac{\sum_{i=1}^{N}\left(P_{CO_2(i)}^{cal} - P_{CO_2(i)}^{exp}\right)}{\sum_{i=1}^{N}\left(P_{CO_2(i)}^{exp}\right)^2}\right]^{0.5} \tag{38}$$

Modeling of ocean currents in the port of Tanjung Perak Surabaya used Gauss-Markov process, with a maximum current speed varies from 2, 2.25 and 2.5 knots.

III. RESULT AND ANALYSIS

In the present study, gas-liquid equilibria of CO_2-K_2CO_3-MDEA-H_2O system were predicted by electrolyte UNIQUAC model at 30°C and atmospheric pressure with 30% K_2CO_3 and variation of MDEA weight percent 2, 5, 8, and 10%. The simulation was performed by Matlab program. The predicted simulation results were validated accurately using experimental data by Sholichatun and

Finalis [18]. It can be seen in Figure 1 that the predicted simulation results using electrolyte UNIQUAC model with the experimental data show the same profile. It indicates that the model correlated well the experimental data. The deviation of CO_2 partial pressure between calculation with electrolyte UNIQUAC model and experimental data is 14.85%. To reduce the deviation, the ion component of H_3O^+, OH^-, and $MDEAH^+$ may be calculated and the energy interaction parameter of these components may also be fitted by experimental data.

The energy interaction parameters of electrolyte UNIQUAC model can be seen in Table 1. Activity coefficient is needed to calculate the phase equilibrium. To apply the electrolyte UNIQUAC model for calculating the activity coefficient in liquid phase, it is required to obtain the energy interaction parameter for molecule-molecule, molecule-ion pair, and ion pair-molecule by fitting with the experimental data. If the energy interaction parameter, τ_{kl}, is positive, the empirical parameter, ψ_{kl}, will increase with increasing temperature. Otherwise, if the energy interaction parameter is negative, the empirical parameter will decrease with increasing temperature.

Figure 2 represents the CO_2 partial pressure calculation of the simulation program. The figure shows CO_2 loading increases with increasing of CO_2 partial pressure. At the same CO_2 partial pressure, CO_2 loading will also increase with the increase of MDEA weight percent. CO_2 loading is the total amount of CO_2 absorbed divided by the amount of K^+ and MDEA. MDEA is an activator, it can accelerate the CO_2 absorb in the solution, thus the CO_2 loading will increase. Furthermore, to obtain the same CO_2 loading, it is required higher partial pressure of CO_2 at lower MDEA composition.

The gas-liquid equilibria data for CO_2-K_2CO_3-MDEA-H_2O system can be seen in Figure 3-11

Figure 3-8 show the relationship between the mole fraction components in the liquid phase and CO_2 loading at varied MDEA concentration. With increasing CO_2 loading, the mole fraction of CO_2 and HCO_3^- in the liquid phase will increase and the mole fraction of CO_3^{2-} will decrease. In addition, with the increase of CO_2 loading, the mole fraction of H_2O, K^+ and MDEA only decrease slightly. From these Figure, it can be seen that with the addition of MDEA concentration, it can enhance the CO_2 loading and the mole fraction components in the liquid phase, except the mole fraction of H_2O. The H_2O mole fraction will decrease with increasing MDEA concentration. Because with the increase of MDEA concentration, the CO_2 absorbed and the amount of MDEA in the solution will increase, thus the H_2O mole fraction in the solution will decrease. The amount of CO_2 absorbed is the amount of CO_2 reacted and CO_2 dissolved in the solution. The greater CO_2 loading, the greater CO_2 reacted and dissolved in the solution. Thus, the amount of CO_2 in the liquid phase and HCO_3^- formed will also increase, and the amount of CO_3^{2-} consumed will decrease. In chemical absorption process, MDEA serves as a promotor that accelerates the reaction of K_2CO_3 with CO_2 gas, thus the increase of MDEA weight percent in K_2CO_3 aqueous solution will be followed by increasing CO_2 loading.

Figure 9-11 represent the relationship between the mole fraction components in the gas phase and CO_2 loading at varied MDEA concentration. The mole fraction of CO_2 in gas phase will increase with the increase of CO_2 loading. Otherwise with increasing CO_2 loading, N_2 mole fraction will decrease and H_2O mole fraction will decrease slightly. Mole fraction in the gas phase is equilibrium with mole fraction in the liquid phase. Thus, the greater mole fraction a component in the liquid phase, the greater mole fraction in the gas phase. These Figure also show the addition of MDEA concentration can enhance the CO_2 loading and the mole fraction components in the gas phase, except the H_2O mole fraction. The mole fraction of H_2O in the gas phase will decrease with the increase of MDEA weight percent.

IV. CONCLUSION

The model to predict gas-liquid equilibria data of CO_2-K_2CO_3-MDEA-H_2O system have been developed in the present study at 30^oC and atmospheric pressure with 30% of potassium carbonate and 2, 5, 8, 10% of MDEA by electrolyte UNIQUAC model. The predicted simulation results were validated accurately using experimental data by Sholichatun and Finalis [18]. And the electrolyte UNIQUAC model correlated well the experimental data. The calculated and experimental CO_2 partial pressure deviation is 14.85%. The energy interaction parameters of electrolyte UNIQUAC model were obtained by Least Square method. With the increase of CO_2 partial pressure, the CO_2 loading increased. At the same CO_2 partial pressure, CO_2 loading increased with increasing MDEA weight percent. The mole fraction of CO_2 and HCO_3^- in the liquid phase increased and the mole fraction of CO_3^{2-} decreased with the increase of CO_2 loading. Mole fraction in the gas phase is equilibrium with mole fraction in the liquid phase. The greater mole fraction a component in the liquid phase, the greater mole fraction in the gas phase. The gas-liquid equilibria data obtained in the present study can be used as a reference for designing CO_2 absorption column in industries.

NOMENCLATURE

d_k	Density of component k in kg/m^3
H	Henry constant in Pa
I	*Ionic strength* in mol/kg
K	Equilibrium constant
M_k	Molecular weight of component k in kg/mol
n	Total mole in the solution
P	Pressure in Pa
q	Surface area parameter
r	Volume parameter volume
R	Gas constant in Joule/mol.K
T	Temperature in Kelvin
$\bar{v}$	Partial molar volume in m^3/mol
x_i	Mole fraction in the liquid phase
x_k	Mole fraction of component k
x'_k	Mole fraction of component k in free ion
y_i	Mole fraction in the gas phase
z_i	Charge number of ion i

Greek letters

γ	Activity coefficient
ε	Dielectric constant
θ	Area fraction
λ	Lagrange multiplier
μ	Chemical potential
τ	The energy interaction parameter
φ	Fugacity coefficient
ϕ	Volume fraction

Subscript

a	Anion
c	Cation
i	Ion
k	Element
m	Molecular solute
n	Solvent
tot	Total
w	Water

Superscript

C	Combinatorial
cal	Calculated
dh	Debye-Huckel
exp	Experimental
R	Residual
s	Saturated
w	Water
∞	Infinite dilution in water
*	Assymetric

REFERENCES

[1]. Anand B Rao and Edward S Rubin, "A Technical, Economic, and Environmental Assessment of Amine-based CO2 Capture Technology for Power Plant Greenhouse Gas Control.," *Environmental, Science, & Technology*, vol. 36, no. 20, pp. 4467-4475, September 2002.

[2]. Hongyi Dang and Gary T Rochelle, "CO2 absorption rate and solubility in monoethanolamine/piperazine/water," in *The First National Conference on Carbon Sequestration*, Washington, DC, 2001.

[3]. John Timothy Cullinane, "Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption," University of Texas, Austin, PhD Dissertation 2005.

[4]. Sander Bo, Aage Fredenslund, and Peter Rasmussen, "Calculation of Vapour-Liquid Equilibria in Mixed Solvent/salt Systems using an Extended UNIQUAC Equation," *Chemical Engineering Science*, vol. 41, no. 5, pp. 1171-1183, 1968.

[5]. David M Austgen, Gary T Rochelle, Xiao Peng, and Chau- Chyun Chen, "Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems Using the Electrolyte-NRTL Equation," *Industrial & Engineering Chemistry Research*, vol. 28, no. 7, pp. 1060-1073, July 1989.

[6]. Mark L Posey, "Thermodynamics Model for Acid Gas Loaded Aqueous Alkanolamine Solutions," University of Texas, Austin, PhD Dissertation 1996.

[7]. Marcus D Hilliard, "A Predictive Model for Aqueous Potassium Carbonate, Piperazine, Monoethanolamine for Carbon Dioxide Removal from Flue Gas," University of Texas, Austin, PhD Dissertation 2008.

[8]. A Benamor and M K Aroua, "Modeling of CO2 Solubility and Carbamate Concentration in DEA, MDEA and Their Mixtures Using The Deshmukh-Mather Model," *Fluid Phase Equilibria*, vol. 231, no. 2, pp. 150-162, April 2005.

[9]. Hawar A M Haider, Rozita Yusoff, and M K Aroua, "Equilibrium Solubility of Carbondioxide in 2(Methylamino)ethanol," *Fluid Phase Equilibria*, vol. 303, no. 2, pp. 162-167, April 2011.

[10]. Saeid Kamalpour and Amine Mehablia, "Thermodynamics of CO2-MDEA using eNRTL with Differential Evolution Algorithm," *International Journal of Thermodynamics (IJoT)*, vol. 15, no. 3, pp. 157-168, June 2012.

[11]. H E Benson, J H Field, and W P Haynes, "Improved Process for CO2 Absorption Uses Hot Carbonate Solutions," *Chemical Engineering Progress*, vol. 52, no. 10, pp. 433-438, 1956.

[12]. Gianni Astarita, David W Savage, and John M Longo, "Promotion of CO2 mass transfer in carbonate solutions," *Chemical Engineering Science*, vol. 36, no. 3, pp. 581-588, 1981.

[13]. R K Bartoo, T M Gemborys, and C W Wolf, "Recent Improvements to the Benfield Process Extend its Use," in *Nitrogen '91 Conference*, Copenhagen, Denmark., 1991.

[14]. D W Savage, G Sartori, and G Astarita, "Amines as Rate Promoters for Carbon Dioxide Hydrolysis," *Faraday Discussion of The Chemical Society*, vol. 77, pp. 17-31, 1984.

[15]. M R Rahimpour and A Z Kashkooli, "Enhanced Carbon Dioxide Removal by Promoted Hot Potassium Carbonate in a Split-Flow Absorber," *Chemical Engineering Processing : Process Intensification*, vol. 43, no. 7, pp. 857-856, July 2004.

[16]. J Tim Cullinane and Gary T Rochelle, "Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine," *Chemical Engineering Science*, vol. 59, no. 17, pp. 3619-3630, September 2004.

[17]. John Polasek and Jerry A Bullin, "Selecting amines for Sweetening Units," in *Gas Processors Association (GPA) Regional Meeting,"Process Considerations in Selecting Amine"*, Tulsa, Oklahoma, 1994.

[18]. Sholichatun and E R Finalis, "The Influence of an Additive MDEA on Solubility of CO2 in Aqueous Solution of K2CO3," Institut Teknologi Sepuluh Nopember, Surabaya, Bachelor Final Project 2010.

[19]. L Kaewsichan, "A Vapor-Liquid Equilibrium Model for CO2-H2S-Monoethanolamine-Methyldiethanolamine-Water System using The Electrolyte UNIQUAC Equation," , Colorado School of Mines.," Colorado School of Mines, Goldren, PhD Thesis 1999.

[20]. L Kaewsichan, O Al-Bofersen, Victor F Yesavage, and M Sami Selim, "Predictions of The Solubility of Acid Gases in Monoethanolamine (MEA) and Methyldiethanolamine (MDEA) Solutions using The Electrolyte-UNIQUAC Model," *Fluid Phase Equilibria*, vol. 183-184, pp. 159-171, July 2001.

[21]. M David Austgen, Gary T Rochelle, and Chau C Chen, "Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems. 2. Representation of H2S and CO2 Solubility in Aqueous MDEA and CO2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA," *Industrial & Engineering Chemistry Research*, vol. 30, no. 3, pp. 543-555, March 1991.
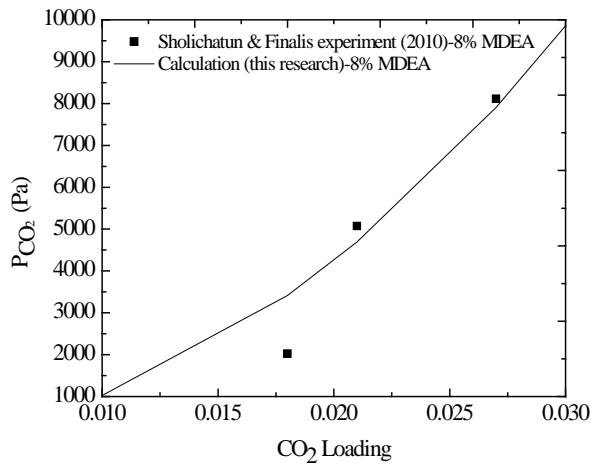
Figure 1. The comparison of predicted simulation results with the experimental data of CO_2-K_2CO_3-MDEA-H_2O system
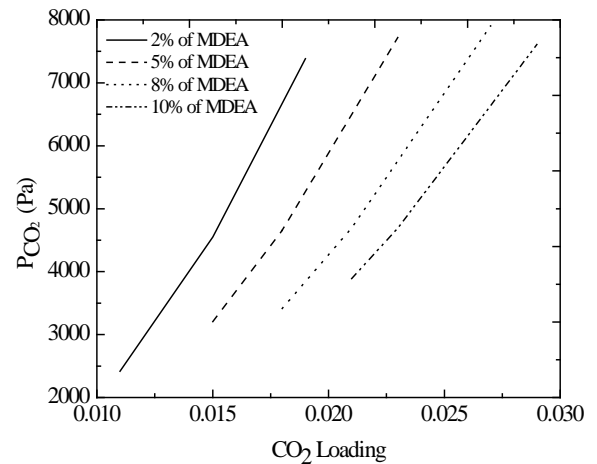

Figure 2. The relationship between CO_2 partial pressure and CO_2 loading with the variation of MDEA weight percent
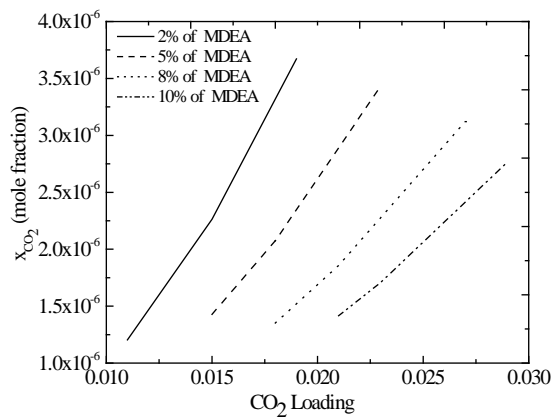

Figure 3. The relationship between CO_2 liquid fraction and CO_2 loading with the variation of MDEA weight percent
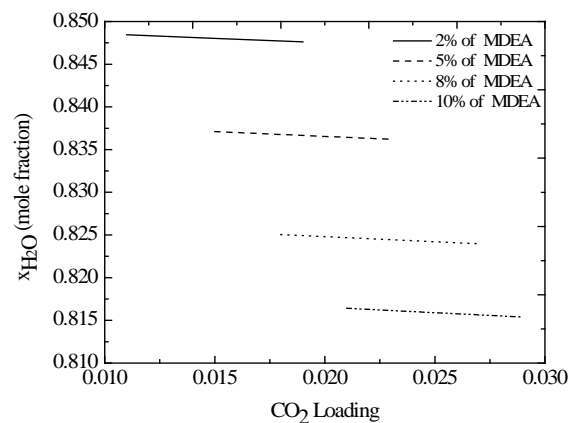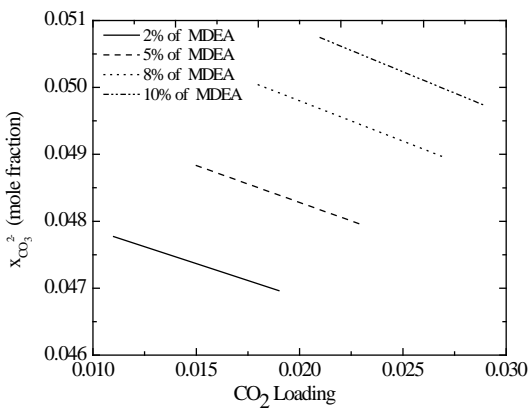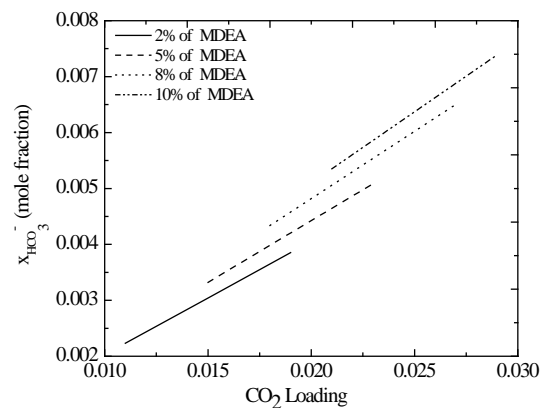

Figure 4. The relationship between H_2O liquid fraction and CO_2 loading with the variation of MDEA weight percent

Figure 5. The relationship between CO_3^{2-} liquid fraction and CO_2 loading with the variation of MDEA weight percent

Figure 6. The relationship between HCO_3^- liquid fraction and CO_2 loading with the variation of MDEA weight percent
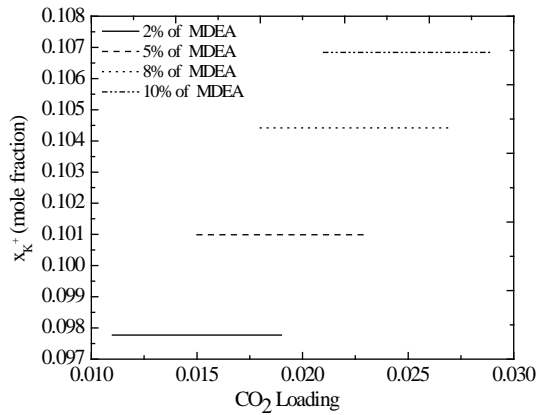
Figure 7. The relationship between K^+ liquid fraction and CO_2 loading with the variation of MDEA weight percent
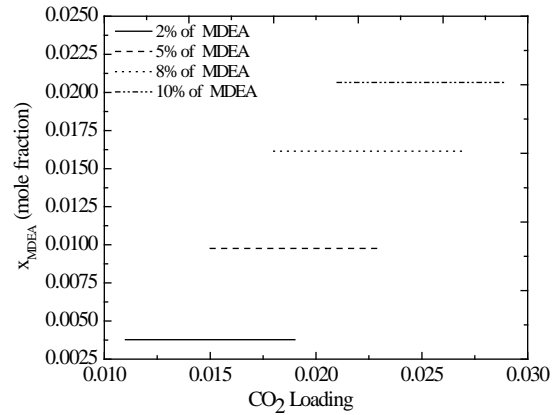

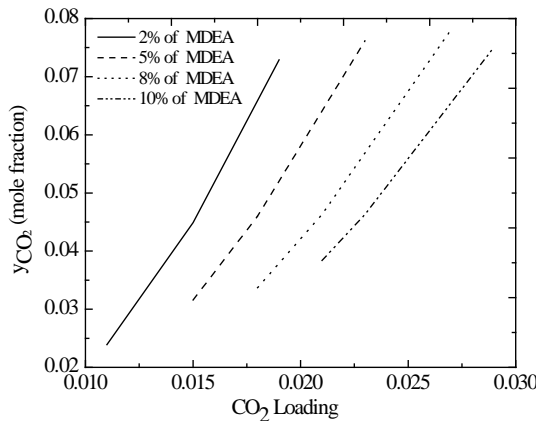Figure 8. The relationship between MDEA liquid fraction and CO_2 loading with the variation of MDEA weight percent

Figure 9. The relationship between CO_2 gas fraction and CO_2 loading with the variation of MDEA weight percent
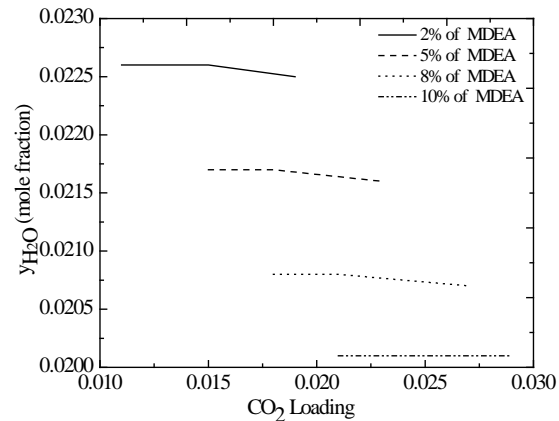

Figure 10. The relationship between H_2O gas fraction and CO_2 loading with the variation of MDEA weight percent
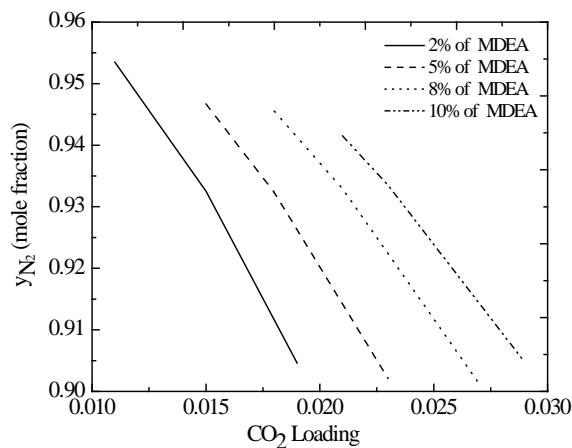

Figure 11. The relationship between N_2 gas fraction and CO_2 loading with the variation of MDEA weight percent

TABLE 1.
THE ENERGY INTERACTION PARAMETERS OF ELECTROLYTE UNIQUAC MODEL

Interaction Pair	Energy Interaction Parameter (τ)
$\tau_{H_2O-K^+,HCO_3^-}$	-372
$\tau_{H_2O-K^+,CO_3^{2-}}$	-2405
$\tau_{K^+,HCO_3^--H_2O}$	-627
$\tau_{K^+,CO_3^{2-}-H_2O}$	-661
$\tau_{K^+,HCO_3^--CO_2}$	-965
$\tau_{K^+,CO_3^{2-}-CO_2}$	-1491
τ_{K^+,HCO_3^--MDEA}	-517
$\tau_{K^+,CO_3^{2-}-MDEA}$	-580.55
$\tau_{CO_2-K^+,HCO_3^-}$	-50.4
τ_{MDEA-K^+,HCO_3^-}	-1054.68
$\tau_{CO_2-K^+,CO_3^{2-}}$	-551.2
$\tau_{MDEA-K^+,CO_3^{2-}}$	-730