Prediction of Gas-Liquid Equilibria of CO₂- K₂CO₃-MDEA-H₂O System by Electrolyte UNIQUAC Model

Saidah Altway¹, Kuswandi¹, Ali Altway¹

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 CO₂ from the gas stream. Chemical absorption is the most economical method for CO₂ separation. One of the processes that is widely used in industries is Benfield process with K₂CO₃ (potassium carbonate) as a solvent and amine as a promoter. In this study, MDEA (Methyldiethanolamine) is used as a promoter. As a reference for designing CO₂ 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 CO₂-K₂CO₃-MDEA-H₂O system at 30°C and atmospheric pressure with 30% K₂CO₃ 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 CO₂ 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 CO₂ partial pressure, CO₂ loading increased, and also at the same partial pressure of CO₂, CO₂ loading increased with the increase of weight percent of MDEA.

Keywords — Electrolyte UNIQUAC Model, Energy Interaction Parameter, Gas-liquid Equilibria, Methyldiethanolamine

I. INTRODUCTION

Carbon dioxide (CO₂) has to be removed from the gas stream, since CO₂ induces several losses in industries. CO₂ is an acid gas which is corrosive and it causes damage the plant utility and the piping system. In the natural gas liquefaction process, CO₂ 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 CO₂ gas will reduce the heating value of combustion. In the ammonia synthesis unit, CO₂ is a poison to the catalyst. Hence it is necessary to reduce CO₂ from the gas stream. Various processes can be used for CO₂ separation. Rao and Rubin [1] represented that there are several technology in CO₂ capture, such as cryogenic, membrane, adsorption, and the most economical method for CO₂ separation is chemical absorption.

Dang and Rochelle [2] indicated that energy consumption for solvent regeneration is the biggest cost factor for CO₂ capture, which can reach 49% of the total cost of CO₂ capture. Furthermore, another factor is the solvent capacity which can specify the total amount of CO₂ absorbed per unit of solvent. Wide variety of solvents can be used in the gas processing to separate CO₂ gas, however Cullinane [3] showed that potassium carbonate and alkanolamine are the most effective solvents.


Potassium carbonate (K₂CO₃) 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°C 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
improve the overall performance of solvents and increase the absorption rate of CO₂, it can be used Benfield process, which uses alkanolamine as a promotor in K₂CO₃ 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 CO₂, pressure with 30% K₂CO₃ and variation of 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 CO₂-K₂CO₃-MDEA-H₂O system at 30°C and atmospheric pressure with 30% K₂CO₃ and variation of weight percent of MDEA 2, 5, 8, and 10% by electrolyte UNIQUAC model. The simulation was conducted using Matlab version 6. The energy interaction parameters of electrolyte UNIQUAC model were obtained using Matlab programming. From the reaction above, the element balances as follows:

\[ 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \text{K1} \]
\[ \text{CO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^- \text{K2} \]
\[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \text{K3} \]
\[ \text{MDEA}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{MDEA} \text{K4} \]

Components calculated in this study are H₂O, CO₂, MDEA, K⁺, CO₃²⁻, and HCO₃⁻. While H₂O, OH⁻, and MDEA⁺ are ignored because the value are very small. From the reaction above, the element balances as follows:

\[ 2x_{\text{H}_2\text{O}} + x_{\text{HCO}_3^-} - \frac{n_{\text{Htot}}}{n_{\text{tot}}} = 0 \]  \hspace{1cm} (1)
\[ x_{\text{CO}_2} + 2x_{\text{CO}_3^{2-}} + x_{\text{HCO}_3^-} - \frac{n_{\text{Htot}}}{n_{\text{tot}}} = 0 \]  \hspace{1cm} (2)
\[ x_{\text{H}_2\text{O}} + 2x_{\text{CO}_2} + 3x_{\text{CO}_3^{2-}} + 3x_{\text{HCO}_3^-} - \frac{n_{\text{tot}}}{n_{\text{tot}}} = 0 \]  \hspace{1cm} (3)
\[ x_{\text{MDEA}} - \frac{n_{\text{MDEAtot}}}{n_{\text{tot}}} = 0 \]  \hspace{1cm} (4)
\[ x_{K^+} - \frac{n_{K^+\text{tot}}}{n_{\text{tot}}} = 0 \]  \hspace{1cm} (5)

The Lagrange multiplier \((\lambda_k)\) is used for each element, thus the chemical potential for each component is as follows:

\[ \mu_{\text{H}_2\text{O}} - 2\psi_H - \psi_O = 0 \]  \hspace{1cm} (6)
\[ \mu_{\text{CO}_2} - \psi_c - 2\psi_O = 0 \]  \hspace{1cm} (7)
\[ \mu_{\text{HCO}_3^-} - 2\psi_H - \psi_O = 0 \]  \hspace{1cm} (8)

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

\[ \ln K = C_1 + C_2 \frac{T}{N} + C_3 \ln T + C_4 T \]  \hspace{1cm} (14)

Thus the standard chemical potential \(\mu^o\) can be calculated from the equilibrium constant K:

\[ RT \ln K_j = - \sum_{i=1}^{N} p_{ij} \mu^o_i \text{ j =1,2,...,R} \]  \hspace{1cm} (15)

Activity coefficient, \(\gamma_i\), is the correction of chemical potential for ideal solution, as the effect of non-ideal solution characteristics.

From Equation (1) – Equation (12), there are 12 equations with 12 unknown variables such as \(x_{\text{H}_2\text{O}}, x_{\text{CO}_2}, x_{\text{MDEA}}, x_{\text{CO}_3^{2-}}, x_{K^+}, \psi_H, \psi_O, \psi_{K}, \psi_{MDEA}\) and the total moles in the liquid phase, \(n_{\text{tot}}\).

The simultaneous equations above are calculated by Newton Raphson method and the activity coefficients \(\gamma_i\) are calculated using electrolyte UNIQUAC model, with the initial setting \(\gamma_i = 1\), till the values of \(x_i\) and \(\gamma_i\) 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-Hückel 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 m:
\[
\ln \gamma_m = \ln \gamma_m^{dh} + \ln \gamma_m^{C} + \ln \gamma_m^{R}
\]  

For molecular solute m:
\[
\ln \gamma_m' = \ln \gamma_m^{dh} + \ln \gamma_m^{\star C} + \ln \gamma_m^{\star R}
\]

For ionic component i:
\[
\ln \gamma_i' = \ln \gamma_i^{dh} + \ln \gamma_i^{\star C} + \ln \gamma_i^{\star R}
\]

Where:
\[
\gamma_i^{\star R} = \frac{24\mu_i\omega_i}{\varrho_i} \left[ 1 + b\sqrt{I} - \frac{1}{1 + b\sqrt{I}} - 2\ln 1 + b\sqrt{I} \right]
\]

\[
\ln \gamma_i^{\star dh} = \ln \gamma_i^{dh} + \ln \gamma_i^{\star R}
\]

The residual activity coefficient of ions are related to the residual activity coefficient of ion pairs which are appropriate as follows:
\[
\ln \gamma_{a,c,a}^{\star R} = \frac{a_d}{a_d + c_a} \ln \gamma_a^{\star R} + \frac{a_d}{a_d + c_a} \ln \gamma_a^{\star R} + \frac{a_d}{a_d + c_a} \ln \gamma_a^{\star R}
\]  

To solve Equation (28), it can be assumed for each ion pair \( \gamma_i^{\star R} \) is equal \( \gamma_i^{\star R} \) as given in Equation (29).
\[
\ln \gamma_{a,c,a}^{\star R} = \ln \gamma_a^{\star R} = \ln \gamma_a^{\star R}
\]

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:
\[
\langle \ln \gamma_i^{\star R} \rangle = \sum_a \left( \frac{\theta_a c_{a,c,a} \gamma_a^{\star R}}{\Sigma \theta_a c_{a,c,a} \gamma_a^{\star R}} \right) \ln \gamma_i^{\star R}
\]

After the composition in the liquid phase \( x_i \) and the activity coefficient \( \gamma_i \) have been obtained, the partial pressure and the composition of CO2 in the gas phase can be calculated from the following equation:
\[
P_{CO_2} = x_{CO_2} H_{CO_2}
\]

\[
\gamma_{CO_2} = \frac{P_{CO_2}}{P_{CO_2}}
\]

\( H_{CO_2} \) is the Henry constant of CO2 in the solution associated with \( H_{CO_2}^w \). Henry constant of CO2 in pure water through the activity coefficient \( \gamma_i \):
\[
H_{CO_2} = \gamma_{CO_2} H_{CO_2}^w
\]

Henry constant of CO2 in pure water is determined from the following correlation equation [21]:
\[
\ln H_{CO_2} = 170.7126 - \frac{847.7717}{T} - 21.95743 T + 0.005781 T
\]

Whereas the partial pressure and the composition of H2O in the gas phase can be calculated by the Equation (36) and (37) as follows:
\[
P_{H_2O} = x_{H_2O} y_{H_2O} P_{H_2O}^f
\]

\[\gamma_{H_2O} = \frac{P_{H_2O}}{P_{tot}}
\]

\( P_{H_2O}^f \) is the saturated pressure of H2O and \( P_{tot} \) is the total pressure.

The deviation of calculated and experimental CO2 partial pressure was calculated as follows:
\[
Error = \frac{\gamma_{i,n=1}^N \left( \frac{P_{exp}(CO_2)}{P_{Calc}(CO_2)} \right)}{\sum_{i=1}^N \left( \frac{P_{exp}(CO_2)}{P_{Calc}(CO_2)} \right)^{0.5}}
\]

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 CO2-K2CO3-MDEA-H2O system were predicted by electrolyte UNIQUAC model at 30°C and atmospheric pressure with 30% K2CO3 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 Sholichtun 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 CO2 partial pressure between calculation with electrolyte UNIQUAC model and experimental data is 14.85%. To reduce the deviation, the ion component of \( \text{H}_2\text{O}^+ \), \( \text{OH}^- \), and \( \text{MDEA}^+ \) 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, \( \tau_{kl} \), is positive, the empirical parameter, \( \psi_{kl} \), 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 CO2 partial pressure calculation of the simulation program. The figure shows CO2 loading increases with increasing of CO2 partial pressure. At the same CO2 partial pressure, CO2 loading will also increase with the increase of MDEA weight percent. CO2 loading is the total amount of CO2 absorbed divided by the amount of K2CO3 and MDEA. MDEA is an activator, it can accelerate the CO2 absorb in the solution, thus the CO2 loading will increase. Furthermore, to obtain the same CO2 loading, it is required higher partial pressure of CO2 at lower MDEA composition.

The gas-liquid equilibria data for CO2-K2CO3-MDEA-H2O system can be seen in Figure 3-11. Figure 3-8 show the relationship between the mole fraction components in the liquid phase and CO2 loading at varied MDEA concentration. With increasing CO2 loading, the mole fraction of CO2 and HCO3- in the liquid phase will increase and the mole fraction of CO3 2- will decrease. In addition, with the increase of CO2 loading, the mole fraction of H2O, \( K^- \) and MDEA only decrease slightly. From these Figure, it can be seen that with the addition of MDEA concentration, it can enhance the CO2 loading and the mole fraction components in the liquid phase, except the mole fraction of H2O. The H2O mole fraction will decrease with increasing MDEA concentration. Because with the increase of MDEA concentration, the CO2 absorbed and the amount of MDEA in the solution will increase, thus the H2O mole fraction in the solution will decrease. The amount of CO2 absorbed is the amount of CO2 reacted and CO2 dissolved in the solution. The greater CO2 loading, the greater CO2 reacted and dissolved in the solution. Thus, the amount of CO2 in the liquid phase and HCO3- formed will also increase, and the amount of CO3 2- consumed will decrease. In chemical absorption process, MDEA serves as a promotor that accelerates the reaction of K2CO3 with CO2 gas, thus the increase of MDEA weight percent in K2CO3 aqueous solution will be followed by increasing CO2 loading.

**IV. CONCLUSION**

The model to predict gas-liquid equilibria data of CO2-K2CO3-MDEA-H2O system have been developed in the present study at 30°C 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 CO2 partial pressure deviation is 14.85%. The energy interaction parameters of electrolyte UNIQUAC model were obtained by Least Square method. With the increase of CO2 partial pressure, the CO2 loading increased. At the same CO2 partial pressure, CO2 loading increased with increasing MDEA weight percent. The mole fraction of CO2 and HCO3- in the liquid phase increased and the mole fraction of CO3 2- decreased with the increase of CO2 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 CO2 absorption column in industries.

**NOMENCLATURE**

- \( d_k \): Density of component \( k \) in kg/m³
- \( H \): 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
- \( V \): Partial molar volume in m³/mol
- \( x_i \): Mole fraction in the liquid phase
- \( x_k \): Mole fraction of component \( k \)
- \( y_i \): Mole fraction in the gas phase
- \( z_i \): Charge number of ion i

Figure 9-11 represent the relationship between the mole fraction components in the gas phase and CO2 loading at varied MDEA concentration. The mole fraction of CO2 in gas phase will increase with the increase of CO2 loading. Otherwise with increasing CO2 loading, N2 mole fraction will decrease and H2O 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 CO2 loading and the mole fraction components in the gas phase, except the H2O mole fraction. The mole fraction of H2O in the gas phase will decrease with the increase of MDEA weight percent.
REFERENCES


Figure 1. The comparison of predicted simulation results with the experimental data of CO₂-K₂CO₃-MDEA-H₂O system

Figure 2. The relationship between CO₂ partial pressure and CO₂ loading with the variation of MDEA weight percent

Figure 3. The relationship between CO₂ liquid fraction and CO₂ loading with the variation of MDEA weight percent

Figure 4. The relationship between H₂O liquid fraction and CO₂ loading with the variation of MDEA weight percent

Figure 5. The relationship between CO₃²⁻ liquid fraction and CO₂ loading with the variation of MDEA weight percent

Figure 6. The relationship between HCO₃⁻ liquid fraction and CO₂ loading with the variation of MDEA weight percent
TABLE 1.

THE ENERGY INTERACTION PARAMETERS OF ELECTROLYTE UNIQVAC MODEL

<table>
<thead>
<tr>
<th>Interaction Pair</th>
<th>Energy Interaction Parameter (τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$τ_{H_2O-K^+,HCO_3^-}$</td>
<td>-372</td>
</tr>
<tr>
<td>$τ_{H_2O-K^+,CO_3^{2-}}$</td>
<td>-2405</td>
</tr>
<tr>
<td>$τ_{K^+,HCO_3^-−H_2O}$</td>
<td>-627</td>
</tr>
<tr>
<td>$τ_{K^+,CO_3^{2-}−H_2O}$</td>
<td>-661</td>
</tr>
<tr>
<td>$τ_{K^+,HCO_3^-−CO_2}$</td>
<td>-965</td>
</tr>
<tr>
<td>$τ_{K^+,CO_3^{2-}−CO_2}$</td>
<td>-1491</td>
</tr>
<tr>
<td>$τ_{K^+,HCO_3^-−MDEA}$</td>
<td>-517</td>
</tr>
<tr>
<td>$τ_{K^+,CO_3^{2-}−MDEA}$</td>
<td>-580.55</td>
</tr>
<tr>
<td>$τ_{CO_2−K^+,HCO_3^-}$</td>
<td>-50.4</td>
</tr>
<tr>
<td>$τ_{MDEA−K^+,HCO_3^-}$</td>
<td>-1054.68</td>
</tr>
<tr>
<td>$τ_{CO_2−K^+,CO_3^{2-}}$</td>
<td>-551.2</td>
</tr>
<tr>
<td>$τ_{MDEA−K^+,CO_3^{2-}}$</td>
<td>-730</td>
</tr>
</tbody>
</table>