Thermodynamic Modeling the Solubility of CO\textsubscript{2} in Aqua System of Methyldiethanolamine and 2-(2-Aminoethylamino)ethanol Using the Nonelectrolyte Wilson Nonrandom Factor

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**Abstract**

Alkanolamines are used to remove acidic gases such as CO\textsubscript{2} and H\textsubscript{2}S from natural gas. In this study, thermodynamic modeling of the binary component CO\textsubscript{2}+MDEA, three component MDEA+H\textsubscript{2}O+CO\textsubscript{2} and the quaternary MDEA+AEEA+H\textsubscript{2}O+CO\textsubscript{2} systems were developed using an additional Gibbs argillic model for the first time in the modeling of CO\textsubscript{2} solubility in different solutions. The appropriate model was considered using the assumption of an entirely molecular system without any occurrence of chemical reactions and saturated gas phase from the CO\textsubscript{2} gas. The nonelectrolyte Wilson nonrandom factor (N-Wilson-NRF) model and the activity coefficient method (γ_φ Aproach) were used to calculate solubility of CO\textsubscript{2}. The two-component water- CO\textsubscript{2} model was modeled and the results were obtained by the accuracy of 1.38 of experimental results. In a three-component, water-CO\textsubscript{2}-MDEA-AEEA system with the amount of 6.913, the optimization was developed. The quaternary water-CO\textsubscript{2}-MDEA-AEEA system was optimized with an overall approximation of 19.537 for all experiment data.

**1. INTRODUCTION**

The removal of CO\textsubscript{2} and H\textsubscript{2}S from the flue gas is essential in the process of natural gas purification. In addition, for the design and construction of gas transport equipment, experimental data on the solubility of CO\textsubscript{2} and H\textsubscript{2}S in aquatic alkanolamines are required [1]. Due to the weakness or power of various alkanolamines in absorption of various acid gases, the choice of a suitable combination of these materials in the process of natural gas purification has been studied [2-4]. Also, at wide range of temperatures and pressures, various experiments are carried out to obtain a suitable thermodynamic model for desired estimation of experimental data [5-7]. It became clear that, because of the ionization of these mixtures, the models that utilize the activity coefficient have been used extensively in research projects [8-10]. Typically, in these models, various equations have been used to predict wide-range of interactions using the Pitzer-Debye-Huckel method and narrow-range of interactions using other types of methods [11-13]. Separation factor is an important feature in the choice of alkanolamine solution to eliminate acidic gas or to interpret the kinetic mechanism of acidic absorption in alkanolamine solution. Recently, Barzagli et al. [14] have studied CO\textsubscript{2} absorption and desorption experiments with alkanolamine mixtures in non-aqueous solvents (ethylene glycol mixtures and 2,1 propanediol with methanol or ethanol) [13]. They reported relatively low separation temperature (about 80°C) and less

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2. THERMODYNAMIC MODELING

In this work, we have used gamma-phi (γ-φ) method for modeling the behavior of under investigation systems. Specifically, to calculate the activity coefficients of the components in the gas phase, the N-Wilson-NRF state equation and to calculate the fugacity coefficients in the liquid phase, the Peng Robinson equation has been used [16]. Using the qualitative properties (PVT), we can calculate all thermodynamic properties and thermodynamic potential energies. Here, we will investigate the behavior of PVT of a pure substance in gas and liquid states.

Parameters (a and b) which are called gravity and repulsion parameters, respectively. Here, k1 and k2 are numerical constants that obtained by the critical properties for each pure substance.

Peng-Robinson presented his equation as follows Equation (2) where k1=2 and k2=-1 [17]:

\[
P = \frac{RT}{v-b} - \frac{a(T, \omega)}{v(v+b)+b(v-b)}
\]

(1)

In this equation, a, b are:

\[
a = 0.457235 \frac{RT^2}{P_c}, \quad b = 0.077796 \frac{RT}{P_c}
\]

The k equation is obtained by fitting steam pressure data from boiling point to critical point in Equation (2):

\[
k = 0.37464 + 1.54226\omega - 0.26993\omega^2
\]

(2)

The cubic equations of state for the blends are written as follows in Equation (3):

\[
P = \frac{RT}{v-b} - \frac{a(T, \omega)}{v^2 + k_1by + k_2b^2}
\]

(3)

Also, V is the molar volume of the mixture. In this case, using the mixing rule, the values of a and b can be set according to the ai and bi parameters for the pure substance.

2. 1. Mixture Fugacity Coefficient Using Peng-Robinson Equation

The Peng-Robinson equation of state can be divided as follows in Equation (4) [8-9]:

\[
P = \frac{RT}{v-b} - \frac{a(T, \omega)}{(v+(1+\sqrt{2})b)(v+(1-\sqrt{2})b)}
\]

(4)

By proper derivation from Equation (2), the fugacity coefficient of component i is obtained as follows in Equation (5):

\[
\ln \phi_i = \frac{b_i(Z-B)}{b_i(Z+B)} - \frac{A}{2 B} \frac{\sum_{j} \frac{y_j b_j}{b_i} \ln(Z+B(1+\sqrt{2})) - b_i \ln(Z+B(1-\sqrt{2}))}{a_i}
\]

(5)

2. 2. An Integral Method for the Calculations of Vapor-liquid Equilibrium

In the integral method, the equation of fugacity is used directly for equilibrium calculations. Therefore, for the equilibrium of two phases of vapor and liquid, the equation of fugacity is used based on the following Equation (6) [18, 19]:

\[
f_i = f_i^L
\]

(6)

In this case, the following two methods are proposed for the calculations of vapor-liquid equilibrium, each method depending on the nature of the components:

I. The equation of state approach (φ-φ Approach)

II. The activity coefficient approach (γ-φ Approach)

In the equation of state approach, the fugacity of each component in the vapor and liquid phases is written as follows:

\[
f_i^L = y_i \phi_i^L P \text{ for vapor and } f_i^L = x_i \phi_i^L P \text{ for liquid}
\]

Here Equation (7):

\[
K_i = \frac{y_i \phi_i^L}{x_i \phi_i^L}
\]

(7)
where \( K_i \) is the ratio of components (K-value) for component \( i \). Therefore, with the proper equation of state, the coefficients of fugacity can be calculated.

The activity coefficient is the quantity that represents the deviation of the non-ideal behavior of liquid mixtures from the ideal behavior of Lewis-Randal. When we have an ideal solution, the activity coefficient is 1 and the fugacity of component \( i \) is ideally written as follows in Equation (8):

\[
f_i^{id} = x_i f_{i,pure}
\]

In other words, liquid solutions can be divided into (ideal dilution solution) and (non-ideal solution). Therefore, in order to calculate the activity coefficients, it is necessary to calculate the first fugacity from the pure material. Therefore, fugacity can be achieved by using a dense phase fugacity in Equation (9):

\[
f_{i,pure} = P_i^{sat} \varphi_i^{sat} \exp\left[\frac{V_i^{eq} (P - P_i^{sat})}{RT}\right]
\]

The saturation fugacity coefficient \( \varphi_i^{sat} \) is obtained at a saturation point at temperature \( T \), which can be calculated using the ratio of the fugacity coefficient for the pure component.

### 2.3. Activity Coefficient in Liquid Solutions

For liquid solutions, the activity coefficient is used as the standard deviation from the ideal state, so for the component in liquid solution and constant temperature it can be written as Equation (10) [20-22]:

\[
\gamma_i = \frac{f_i(T, P, x_i)}{f_i^{LR}(T, P, x_i)} = \frac{f_i(T, P, x_i)}{f_i^{eq}(T, P)}
\]

The Lewis-Randal activity coefficient is used for the solutions in which the components are either dissolved or convergent, in any ratio from dilute to concentrated. On the other hand, some solutions have a positive deviation \( (\gamma_i > 1) \) from the Lewis-Randal law, and others have negative deviations \( (\gamma_i < 1) \). For some solutions, you cannot use the Lewis-Randal activity factor. In this kind of systems, components are not resolved in each other with any ratio. In this case, it is not possible to use the Lewis-Randal activity factor for vapor in the solution. In this case, pure vapor may not be available as a standard solution at system temperature and pressure. Another example is the solubility of electrolytes and polymers in solvents. In this case, the activity coefficient for component \( i \) is defined as Equation (11):

\[
\gamma_i = \frac{f_i(T, P, x_i)}{f_i^{eq}(T, P)}
\]

Thus, for equilibrium calculations in liquid and solid phases, using the gamma-phi method, we need to have a proper function for calculating the activity coefficient of the components in the solution. On the other hand, we know that in order to obtain an appropriate model of the activity coefficient, the Gibbs energy function \( (G^F) \) is necessary for the solution which is shown in Equation (12):

\[
\ln \gamma_i = \frac{\partial (G^F / RT)}{\partial N_i} \bigg|_{T, P, N, x} = \frac{\partial (N_i G^F / RT)}{\partial N_i} \bigg|_{T, P, N, x}
\]

### 2.4. Local Composition Models

The local composition model is a semi-experimental method that derives from the concept of the local composition of molecules in a network. The local composition concept was first introduced by Wilson in 1964 [23].

In 2009, the Haghtalab and Mazloumi present new N-Wilson-NRF model which provided a random mode for each cell based on the literature stated [24]. Local molecular fractions are defined using non-random \( \Gamma_{ij} \) coefficients Equation (13):

\[
x_{ij} - x_i \Gamma_{ij} + \Gamma_{ij} x_i - \sum_{k=1}^{N} x_k \beta_{ki}
\]

\[
\Gamma_{ij} = \Gamma_{ji} / \beta_{ij} \cdot \exp(\frac{h_{ij} - h_{ji}}{ZRT}) = \exp(-\frac{\lambda_{ij}}{Z})
\]

While \( \beta_{ij} \neq \beta_{ji}, \beta_{ii} = 1 \) and \( N \) is the number of components in the system and \( Z \) is the coordination number. Using Equation (13), we can obtain the hyperbolic enthalpy formula for a two-component mixture. Assuming that the temperature is independent of enthalpy Equation (14):

\[
\frac{g^F}{RT} = Z[\Gamma_{ij} (\ln \Gamma_{ij} + x_i \ln \Gamma_{ij} - \sum_{j} x_j \ln (\beta_{ij} \beta_{ji}))]
\]

by deriving the Equation (14), the activity coefficient for a component in a two-component mixture is obtained as Equation (15):

\[
\ln \gamma_i = Z[\ln \Gamma_{ij} + x_i (\Gamma_{ij} - 1) + x_j \ln (\beta_{ij} \beta_{ji})]
\]

The general format of the equations for a multi-component mixture is obtained as Equations (16) and (17):

\[
\frac{g^F}{RT} = Z[\sum_{j} x_i (\ln \Gamma_{ij} + \sum_{j} x_j \ln (\beta_{ij}))]
\]

\[
\ln \gamma_i = Z[\ln \Gamma_{ij} - \sum_{j} x_i (\ln \beta_{ij}) + \sum_{j} x_j \ln (\beta_{ij})]
\]

\[
\lambda_{ij} = (h_{ij} - h_{ji})/RT, \lambda_i = \lambda_{ij} = 0, \beta_{ii} = \beta_{ii} = 1.0
\]

### 2.5. The Process Flowchart of Calculating CO2 Gas Solubility

The general method for calculating the
vapor pressure of each of the various system components using the bubble-pressure calculations flowchart is shown in Figure 1. For higher order systems, these equations for the mixtures can be used [17]. As shown in Figure 1 by the help of laboratory pressure, temperature and composition of the components percentage in the liquid phase, by the initial guess for the system pressure, the simulations can be done, and also the composition of the components in the gas phase and the calculated pressure can be gained using this system. It should be noted that for the two-component and multi-component systems the overall process is the same and for the higher order systems, the classic rules of the hybrid can be used.

3. RESULT AND DISCUSSION

3.1. Quaternary Water-CO$_2$-MDEA-2-2-aminoethyl (amino) ethanol System

One of the most important factors in the design of absorption unit is the solvent material. The most important features of a solvent for absorption are higher absorption speed, better function in absorption process, high net recycling capacity and better chemical stability. In the previous studies [25], researchers measured the rate of CO$_2$ absorption among various amines, which showed that 2-2-Aminoethyl(Amino)Ethanol (AEEA) and (2-Aminoethyl) 1,3-Propandiamine solvents can absorb CO$_2$ more quickly. Ma’mum et al. [26] used a screening test and found that the aqueous solution of AEEA could be used as an absorbent in the process of absorbing CO$_2$ from combustion gases. AEEA has a high absorption rate and net recycling capacity, which is clearly higher than monoethanolamine indexes. Also, this material has also shown its high absorption capacity at higher CO$_2$ loads. Recently, Zoghi et al. [27] investigated the effect of various activators in methyl diethanolamine on the CO$_2$ capture process. They showed that AEEA can greatly increase the rate of CO$_2$ absorption compared with other activators such as Piperazine. The amount of waste lost in the recovery process is another important factor that should be considered in choosing the appropriate solvent. Wilson [28] measured the vapor pressure of AEEA under the temperature of the recovery process (395 K) and showed that AEEA had much lower vapor pressure (959 Pa) than monoethanolamine (15900 Pa). Also, thermodynamic modeling of the equilibrium solubility of acid gases in the process of sweetening and absorbing CO$_2$ gas is another vital point. When acid gases are absorbed in an aqueous solution of alkanolamine, different ionic species are produced by chemical reactions. It makes it difficult to calculate the liquid-vapor balance for aqueous solutions of alkanolamine. In this section, we used the gamma-phi(γ-φ) method and the experimental data of Zoghi experiment [15], to develop a thermodynamically model of the quaternary water-CO$_2$-MDEA-AEEA system. It is important to assume the system physically, in order to reduce the volume of the calculations and to simplify the process of chemical reactions. Based on the results of the above four-component system, the target function was equal to 19,537.

**TABLE 1. Optimized Values of the N-Wilson-NRF Equation for the Quaternary Water-CO$_2$-MDEA-AEEA System**

<table>
<thead>
<tr>
<th>i-j</th>
<th>$\lambda_{ij}$</th>
<th>$a_{ij}$</th>
<th>$b_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$-AEEA</td>
<td>$\lambda_{14}$</td>
<td>-27/8734</td>
<td>-48669/667</td>
</tr>
<tr>
<td>AEEA-CO$_2$</td>
<td>$\lambda_{41}$</td>
<td>-8/3472</td>
<td>-7713/6611</td>
</tr>
<tr>
<td>H$_2$O-AEEA</td>
<td>$\lambda_{24}$</td>
<td>278/2278</td>
<td>-941/2250</td>
</tr>
<tr>
<td>AEEA-H$_2$O</td>
<td>$\lambda_{42}$</td>
<td>8/4826</td>
<td>1323/4516</td>
</tr>
<tr>
<td>MDEA_AEEA</td>
<td>$\lambda_{34}$</td>
<td>5/8430</td>
<td>-62/8829</td>
</tr>
<tr>
<td>AEEA_MDEA</td>
<td>$\lambda_{43}$</td>
<td>2/3283</td>
<td>-221/7266</td>
</tr>
</tbody>
</table>

$$\lambda_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

![Figure 1. The Process Flowchart of Calculating CO$_2$ Gas Solubility in Amine Solutions](image-url)
3.2. Interaction Parameter

In the previous sections and in the equation of activity coefficients, we used equation 17 to calculate the interaction parameters, where two parameters a and b were obtained and optimized simultaneously. In this section, by developing the interaction parameter equation, we examined the effect of this change on the accuracy of the calculations.

The equation of interaction parameter with the three sub-parameters a, b and c is defined in Equation (18):

$$\lambda_i = a_i + b_i \frac{T}{T^*} + c_i \frac{T - T^*}{T} + \ln \frac{T}{T^*}$$

(18)

For the quaternary water-CO$_2$-MDEA-AEEA system, the target function was equal to 19.084 and the values of interaction parameters are shown in Table 3.

<table>
<thead>
<tr>
<th>Loading</th>
<th>Pexp (kPa)</th>
<th>P cal(kPa)</th>
<th>Loading</th>
<th>Pexp(kPa)</th>
<th>P cal(kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308.2(K)</td>
<td>103.3</td>
<td>130.66</td>
<td>0.516</td>
<td>100.7</td>
<td>90.96</td>
</tr>
<tr>
<td>0.735</td>
<td>111.6</td>
<td>140.02</td>
<td>0.544</td>
<td>114.5</td>
<td>114.5</td>
</tr>
<tr>
<td>0.753</td>
<td>146.7</td>
<td>171.0261</td>
<td>0.56</td>
<td>128.3</td>
<td>129.3136</td>
</tr>
<tr>
<td>0.807</td>
<td>187.4</td>
<td>207.4161</td>
<td>0.62</td>
<td>133.5</td>
<td>197.655</td>
</tr>
<tr>
<td>0.832</td>
<td>232.9</td>
<td>240.3064</td>
<td>0.652</td>
<td>163.9</td>
<td>242.6039</td>
</tr>
<tr>
<td>0.862</td>
<td>277.7</td>
<td>240.3064</td>
<td>0.704</td>
<td>249.7</td>
<td>373.8</td>
</tr>
<tr>
<td>0.906</td>
<td>350.6</td>
<td>350.6</td>
<td>0.765</td>
<td>373.8</td>
<td>456.6946</td>
</tr>
<tr>
<td>0.934</td>
<td>483.8</td>
<td>368.2</td>
<td>0.805</td>
<td>456.6946</td>
<td>556.0085</td>
</tr>
<tr>
<td>0.944</td>
<td>746.8</td>
<td>263.113</td>
<td>0.846</td>
<td>793.2</td>
<td>622.862</td>
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<tr>
<td>0.954</td>
<td>908.8</td>
<td>271.57</td>
<td>0.895</td>
<td>1335.3</td>
<td>832.1222</td>
</tr>
<tr>
<td>0.966</td>
<td>1028.2</td>
<td>280.1942</td>
<td>0.885</td>
<td>1165.9</td>
<td>797.5861</td>
</tr>
<tr>
<td>0.974</td>
<td>1254.7</td>
<td>290.766</td>
<td>0.885</td>
<td>1165.9</td>
<td>797.5861</td>
</tr>
<tr>
<td>0.988</td>
<td>1438.8</td>
<td>298.3437</td>
<td>0.885</td>
<td>1165.9</td>
<td>797.5861</td>
</tr>
<tr>
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<td>1652.1</td>
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<td>0.885</td>
<td>1165.9</td>
<td>797.5861</td>
</tr>
<tr>
<td>343.2(K)</td>
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<td>324.6064</td>
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<td>1798.8</td>
<td>976.6611</td>
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<tr>
<td>1.002</td>
<td>324.6064</td>
<td>324.6064</td>
<td>0.934</td>
<td>1798.8</td>
<td>976.6611</td>
</tr>
</tbody>
</table>

TABLE 2. Experimental and Calculated Pressure in the Quaternary Water-CO$_2$-MDEA-AEEA System
TABLE 3. Optimized Values of the N-Wilson-NRF Equation in the Quaternary Water-CO$_2$-MDEA-AEEA System

<table>
<thead>
<tr>
<th>i-j</th>
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<th>$a_{ij}$</th>
<th>$b_{ij}$</th>
<th>$c_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$-AEEA</td>
<td>$\lambda_{14}$</td>
<td>-27/8734</td>
<td>-4866/669</td>
<td>-0/01153</td>
</tr>
<tr>
<td>AEEA-CO$_2$</td>
<td>$\lambda_{41}$</td>
<td>-8/3472</td>
<td>-7713/6611</td>
<td>-0/01552</td>
</tr>
<tr>
<td>H$_2$O-AEEA</td>
<td>$\lambda_{54}$</td>
<td>287/2285</td>
<td>-941/2250</td>
<td>-0/07370</td>
</tr>
<tr>
<td>AEEA-H$_2$O</td>
<td>$\lambda_{42}$</td>
<td>8/4826</td>
<td>1323/4516</td>
<td>-0/01154</td>
</tr>
<tr>
<td>MDEA-AEEA</td>
<td>$\lambda_{34}$</td>
<td>5/8430</td>
<td>-62/8829</td>
<td>0/01758</td>
</tr>
<tr>
<td>AEEA-MDEA</td>
<td>$\lambda_{43}$</td>
<td>2/3283</td>
<td>-221/7266</td>
<td>0/01680</td>
</tr>
</tbody>
</table>

**Figure 2.** Molecular Concentration of CO$_2$ in Aqueous Solution of MDEA+AEEA

4. CONCLUSION AND FUTURE PERSPECTIVE

In this project, the solubility of CO$_2$ gas was investigated in alkanolamine solutions. The N-Wilson-NRF model and the activity coefficient method ($\gamma_\varphi$ Approach) were used to calculate solubility of CO$_2$. The two-component water-CO$_2$ model was modeled and the results were obtained by the accuracy of 1.38 of experimental results. In a three-component, water-CO$_2$-MDEA system with the amount of 6.913, the optimization was developed.

The quaternary water-CO$_2$-MDEA-AEEA system was optimized with an overall approximation of 19.537 for all experiment data. By changing the interaction parameter equation of $\lambda_{ij}$ to the three-parametric equation in the two-component system, the approximation of 6.581 and in the three-component system, 19.084 were obtained. The systems used in this study have made a completely reasonable approximation considering that the solubility modeling of gas in solutions is based on the physical interaction. To make the calculation and mentioned systems more accurate, some suggestions are presented which are:

1. Considering chemical reactions in the liquid phase to improve the accuracy of the model,
2. Performing more experiments at higher temperatures and pressures to obtain more operational data,
3. Using mixing rules in multi-component system computing procedure,
4. Using the equations of electrolyte activation to improve the accuracy of the model.

5. REFERENCES


