Prediction of CO₂ solubility in aqueous solutions of N,N-Diethyl ethanolamine (DEEA): A modified Kent-Eisenberg model approach

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Abstract. A tremendous increase in the carbon dioxide emissions over the last few decades has caused serious environmental concern. The research fraternity is working towards the discovery of novel solvents for carbon dioxide with greater removal efficiency. N,N-Diethyl ethanolamine (DEEA), a tertiary amine which can be prepared from renewable resources, is a potential absorbent for carbon dioxide removal. Determination of the equilibrium characteristics of the system plays a key role in the designing of industrial plants. In this work, the equilibrium solubility of CO₂ in aqueous solutions of DEEA at different temperatures and CO₂ partial pressures has been modeled using the modified Kent-Eisenberg model. The model predicted values were found to be in good agreement with the reported experimental data.

Keywords: Carbon capture, Vapour-Liquid equilibrium, Thermodynamic modeling, N,N-Diethyl ethanolamine, modified Kent-Eisenberg model

1. Introduction
The impact of global warming on the environment is a major issue being raised and discussed amongst all the nations of the world. The prime contributor to global warming are the greenhouse gases, mainly carbon dioxide. Hence, utilization of carbon capture and storage (CCS) techniques is essential to reduce carbon dioxide emissions into the atmosphere. Apart from its environmental threat, carbon dioxide is also undesirable in certain chemical processes [1]. As a result, CCS techniques find wide applications in process industries. Absorption of carbon dioxide in physical and/or chemical solvents is a preferred technique for bulk removal of CO₂. Due to its greater CO₂ removal efficiency, physical absorption enhanced by chemical reaction is most favorable. Since CO₂ is acidic in nature, amine based solvents have gained popularity over the last few decades [2]. Monoethanolamine (MEA), diethanolamine (DEA), N-methyl diethanolamine (MDEA), Piperazine (PZ) are some of the traditionally used amine absorbents [3]. However, pertaining to certain drawbacks of these amines as well as the need for solvents with greater efficacy, the search for newer absorbents is persistent among researchers. A novel amine that can be prepared through a renewable route, N,N-Diethyl ethanolamine (DEEA), is a promising candidate for CO₂ capture [4]. For the design and simulation of a CO₂ absorption column employing an aqueous solution of DEEA, it is essential to determine the vapour-liquid equilibrium at the process conditions. Numerous researchers have studied the equilibrium solubility of CO₂ in aqueous DEEA solutions at different temperatures, CO₂ partial pressures and initial amine concentrations [5-
Thermodynamic models such as Kent-Eisenberg, Deshmukh-Mather and electrolyte non random two liquid (eNRTL) model have been used to validate the experimental data [6,7,9-11]. The Kent-Eisenberg model is simple as it assumes an ideal solution and ideal gas with all the non-idealities included in the temperature-dependent equilibrium constant for the amine reaction [12]. Haji-Sulaiman et al. [13] modified the Kent-Eisenberg model stating that the equilibrium constant is dependent not only on temperature, but also on CO2 partial pressure and total amine concentration. In this work, experimental data for equilibrium CO2 solubility in 2 M and 5 M aqueous DEEA solutions at different temperatures and CO2 partial pressures obtained from literature [5,6] is modeled using the modified Kent-Eisenberg model.

2. Theory
The overall reaction between CO2 and DEEA (represented here as R2R’N, where R is the ethyl group and R’ is the ethanol group) can be given by the base-catalyzed hydration mechanism [14]:

\[
\text{CO}_2 + \text{R}_2\text{R’N} + \text{H}_2\text{O} \rightarrow \text{R}_2\text{R’NH}^+ + \text{HCO}_3^-
\]

(1)

However, the following sets of equations govern the absorption of CO2 in an aqueous solution of DEEA:

\[
\text{R}_2\text{R’NH}^+ \overset{k_1}{\rightarrow} \text{R}_2\text{R’N} + \text{H}^+
\]

(2)

\[
\text{CO}_2 + \text{H}_2\text{O} \overset{k_2}{\rightarrow} \text{HCO}_3^- + \text{H}^+
\]

(3)

\[
\text{H}_2\text{O} \overset{k_3}{\rightarrow} \text{H}^+ + \text{OH}^-
\]

(4)

\[
\text{HCO}_3^- \overset{k_4}{\rightarrow} \text{H}^+ + \text{CO}_3^{2-}
\]

(5)

where equation (2) gives the de-protonation of amine while equations (3)-(5) represent the ionization reactions for different species in the solution. The equilibrium constants for reactions (2)-(5) are given by the following equations:

\[
K_1 = \frac{[\text{H}^+][\text{R}_2\text{R’N}]}{[\text{R}_2\text{R’NH}^+]} \quad (6)
\]

\[
K_2 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2][\text{H}_2\text{O}]} \quad (7)
\]

\[
K_3 = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (8)
\]

\[
K_4 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (9)
\]

where [S] represents the equilibrium concentration of species S in the solution. The concentration of water in the solution is very high and hence can be neglected while using equations (7) and (8). By performing a material and charge balance for the species present in the solution at equilibrium conditions, we get the following equations,

Amine balance:

\[
[R_2R’N]_i = [R_2R’N] + [R_2R’NH^+]
\]

(10)

CO2 balance:

\[
\alpha[R_2R’N]_i = [CO_2] + [HCO_3^-] + [CO_3^{2-}]
\]

(11)

Charge balance:
\[ [H^+] + [R_2R'NH^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \]  
(12)

where \([R_2R'N]_t\) is the total or initial DEEA concentration and \(\alpha\) is the CO\(_2\) loading given as mol CO\(_2\)/mol amine. Using Henry’s law, the relation between partial pressure of CO\(_2\) and its concentration in the solution is given as:

\[ P_{CO_2} = H_{CO_2}[CO_2] \]  
(13)

where \(H_{CO_2}\) is the Henry’s law constant. It has been found that the equilibrium constants \(K_2 - K_4\) and \(H_{CO_2}\) are functions of temperature at infinite dilution [15]. The following correlation gives the dependence of these constants on temperature:

\[ K_i \text{ or } H_{CO_2} = \exp\left(\frac{m}{T} + n \ln T + pT + q\right) \]  
(14)

Values of the coefficients for \(K_2 - K_4\) and \(H_{CO_2}\) were obtained from literature [16]. According to the modified Kent-Eisenberg model, the amine de-protonation constant \(K_1\) is not a function of temperature alone, but also a function of CO\(_2\) partial pressure and total amine concentration. Considering the various factors affecting equilibrium, the amine de-protonation constant is given by:

\[ K_1 = K_1'F_1 \]  
(15)

where \(K_1'\) deals with the effect of temperature, while \(F_1\) deals with the effect of CO\(_2\) partial pressure and total amine concentration. Using the pK\(_a\) values published by Littel et al. [17] for conjugate acid of DEEA at different temperatures, the coefficients of equation (14) were obtained for \(K_1'\). Table 1 gives the values of the coefficients for different equilibrium constants.

| Parameter | \(m\) | \(n\) | \(p\) | \(q\) | Reference |
|-----------|-------|-------|-------|-------|-----------|
| \(K_2\)   | -12092.1 | -36.7816 | 0     | 235.482 | [16]      |
| \(K_3\)   | -13445.9 | -22.4773 | 0     | 140.932 | [16]      |
| \(K_4\)   | -12431.7 | -35.4819 | 0     | 220.067 | [16]      |
| \(H_{CO_2}\) | -6789.04 | -11.4519 | -0.010454 | 94.4914 | [16]      |
| \(K_1'\)  | -1048511.8 | -6746.5 | 10.9  | 38684.2 | This work |

The correlation for \(F_1\) is given by the following equation:

\[ \ln F_1 = \frac{a}{P_{CO_2}} + b \ln P_{CO_2} + cP_{CO_2} + \frac{d}{[R_2R'N]_t} + e \ln[R_2R'N]_t + f[R_2R'N]_t \]  
(16)

3. Modeling

Using equations (7)-(9), (11) and (13), a quadratic expression in terms of hydrogen ion concentration was formulated as under:

\[ A [H^+]^2 + B [H^+] + C = 0 \]  
(17)

\[ A = \alpha_{exp}[R_2R'N]_t - \left(\frac{P_{CO_2}}{H_{CO_2}}\right) \]
where $\alpha_{\text{exp}}$ refers to the experimentally determined values of CO$_2$ loading. Table 2 gives the information regarding the experimental data used for model prediction.

**Table 2. Vapour-liquid equilibrium data of CO$_2$-DEEA-H$_2$O system**

| DEEA Concentration | Temperature (K) | Pressure (kPa) | Number of data points | Reference |
|--------------------|-----------------|----------------|-----------------------|-----------|
| 2 M                | 303             | 0.57 - 5.10    | 7                     | [5]       |
| 2 M, 5 M           | 313, 333, 353   | 0.029 - 19.225 | 68                    | [6]       |

A total of 75 experimental data points were used in this study. The values of the equilibrium constants at the desired temperatures were obtained by substituting the values of coefficients given in Table 1 in equation (14). Solving equation (17), hydrogen ion concentrations in the different solutions at equilibrium were obtained. Concentrations of the other species were determined using the following equations:

\[
[CO_2] = \frac{P_{CO_2}}{H_{CO_2}} \tag{18}
\]

\[
[OH^-] = \frac{K_3}{[H^+]} \tag{19}
\]

\[
[HCO_3^-] = K_2 \frac{[CO_2]}{[H^+]} \tag{20}
\]

\[
[CO_3^{2-}] = K_4 \frac{[HCO_3^-]}{[H^+]} \tag{21}
\]

\[
[R_2R'NH^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{22}
\]

\[
[R_2R'N] = [R_2R'N]_k - [R_2R'NH^+] \tag{23}
\]

Thereafter, $K_1$ values were evaluated using equation (6). Having calculated the values of $K_1$ and $K_1'$, the values of $F_1$ were obtained using equation (15). The $F_1$ values were fitted to the model represented by equation (16) and the values of the coefficients were determined by performing multivariable regression in MS Excel 2016. These values are represented in Table 3.

**Table 3. Regression coefficients for modified Kent-Eisenberg model**

| Coefficient | Value |
|------------|-------|
| $a$        | 0.0395|
| $b$        | -0.3371|
| $c$        | -0.0104|
| $d$        | -4.9482|
New values of $F_1$ were predicted for different CO$_2$ partial pressures at 2 M and 5 M DEEA concentration using the obtained regression coefficients in equation (16). These values were used to determine new values of the amine de-protonation constant $K_1$. Using equations (6)-(10), (12) and (13), a fourth order polynomial in terms of $H^+$ ion concentration was formulated as under:

$$A [H^+]^4 + B [H^+]^3 + C [H^+]^2 + D [H^+] + E = 0$$

$$A = 1$$

$$B = K_1 + [R_2R'N]_t$$

$$C = -K_2 \left( \frac{P_{CO_2}}{H_{CO_2}} \right) - K_3$$

$$D = -2K_2K_4 \left( \frac{P_{CO_2}}{H_{CO_2}} \right) - K_4K_2 \left( \frac{P_{CO_2}}{H_{CO_2}} \right) - K_1K_3$$

$$E = -2K_1K_2K_4 \left( \frac{P_{CO_2}}{H_{CO_2}} \right)$$

The predicted values of $K_1$ were used and the polynomial equation was solved using Scilab 5.4.1 to obtain new values of $H^+$ ion concentration. Calculations using equations (19)-(23) were repeated using the predicted values of $[H^+]$. The CO$_2$ loading values were predicted using the following equation:

$$\alpha_{pred} = \frac{[CO_2]+[HCO_3^-]+[CO_3^{2-}]}{[R_2R'N]_t}$$

The percentage average absolute relative deviation between the experimental and predicted values of $\alpha$ was determined by the following expression:

$$\%\text{AARD} = \left| \frac{\alpha_{pred} - \alpha_{exp}}{\alpha_{exp}} \right| \times 100$$

4. Results and Discussion

Figure 1 shows the parity plots for the fitted parameter of the modified Kent-Eisenberg model (ln $F_1$) and the CO$_2$ loadings (mol CO$_2$/mol DEEA). On account of the vast range of CO$_2$ partial pressures at different temperatures and amine concentrations, along with the errors in experimental observations, a good amount of disparity is observed in the calculated and predicted values of the fitted parameter. However, the effect of this deviation on the predicted values of CO$_2$ loading was much less significant. Overall AARD obtained between the experimental and predicted values of CO$_2$ loading was 20.56%. Arshad [18] reported an AARD value of 22.4% for CO$_2$ partial pressures using the extended UNIQUAC model for 91 experimental data points. So, the results are found to be within the acceptable range. Figure 2 displays the improved Kent-Eisenberg model fit to the experimental data for CO$_2$ loading as a function of CO$_2$ partial pressure. A better fit was observed for equilibrium CO$_2$ solubility in 5 M aqueous DEEA solutions than for that in 2 M aqueous DEEA solutions. The %AARD values for the CO$_2$ loadings in 2 M aqueous DEEA solutions were 32.46, 9.99, 11.41 and 43.37 at 303, 313, 333 and 353 K respectively. In 5 M aqueous DEEA solutions, the %AARD values for CO$_2$ loadings are 14.60,
18.31 and 31.98 at 313, 333 and 353 K respectively. With the exception of 303 K, it is observed that the model prediction is higher at lower temperatures. This may be attributed to the fact that the assumption of ideal behavior of the system in the Kent-Eisenberg model is valid at lower temperatures. Since the experimental data at 303 K is taken from another source [5] as compared to that of the other values [6], the observed discrepancy may also be justified.

Figure 1. Parity plot for (a) Fitted parameter and (b) CO₂ Loading

Figure 2. Equilibrium data vs. model for CO₂ solubility in aqueous solutions of (a) 2 M DEEA and (b) 5 M DEEA

The effect of CO₂ partial pressure on the equilibrium concentration of various species in the solution and pH of the solution for 5 M aqueous solution of DEEA at 313 K is presented in figure 3. The
concentration of dissolved CO\textsubscript{2} increases linearly with pressure according to the Henry’s law. The concentration of the carbonate and bicarbonate ions increases as more CO\textsubscript{2} gets absorbed into the DEEA solution, as does the concentration of DEEAH\textsuperscript{+} ion. The concentration of the hydroxyl ion and correspondingly the pH is found to increase initially up to a certain extent and then decrease. This behavior may be observed since absorption is driven by chemical reaction at lower pressures, while at higher pressures physical absorption is significant.

![Figure 3](image)

**Figure 3.** (a) Concentrations of different species in solution and (b) pH of solution as a function of CO\textsubscript{2} partial pressure in 5 M aqueous DEEA solution at 313 K

5. Conclusions

Equilibrium solubility of CO\textsubscript{2} in 2 M and 5 M aqueous solutions of DEEA at different temperatures and CO\textsubscript{2} partial pressures was modeled using the modified Kent-Eisenberg model. The model was found to predict the equilibrium behavior of CO\textsubscript{2}-DEEA-H\textsubscript{2}O system quite well. AARD of 20.56\% was obtained between the experimental and predicted values of CO\textsubscript{2} loading. Speciation data for equilibrium CO\textsubscript{2} absorption in 5 M DEEA solution at 313 K was also presented.

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