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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

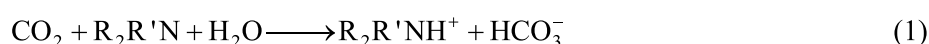
The impact of global warming on the environment is a major issue being raised and discussed amongst all the nations of the world. The prime contributors to global warming are the greenhouse gases, mainly carbon dioxide. Hence, utilization of carbon capture and storage (CCS) techniques is essential to 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-



9]. 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]:



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



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:

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

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

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

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

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:

$$[\text{R}_2\text{R}'\text{N}]_t = [\text{R}_2\text{R}'\text{N}] + [\text{R}_2\text{R}'\text{NH}^+] \quad (10)$$

CO₂ balance:

$$\alpha[\text{R}_2\text{R}'\text{N}]_t = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (11)$$

Charge balance:

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

where $[R_2R'N]_t$ is the total or initial DEEA concentration and α is the CO₂ loading given as mol CO₂/mol amine. Using Henry's law, the relation between partial pressure of CO₂ and its concentration in the solution is given as:

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

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:

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

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 CO₂ partial pressure and total amine concentration. Considering the various factors affecting equilibrium, the amine de-protonation constant is given by:

$$K_1 = K_1' F_1 \quad (15)$$

where K_1' deals with the effect of temperature, while F_1 deals with the effect of CO₂ 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.

Table 1. Values of coefficients of Equation (14)

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:

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

3. Modeling

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

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

$$A = \alpha_{\exp} [R_2R'N]_t - \left(\frac{P_{CO_2}}{H_{CO_2}} \right)$$

$$B = -K_2 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right)$$

$$C = -K_2 K_4 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right)$$

where α_{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_2O 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:

$$[\text{CO}_2] = \frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \quad (18)$$

$$[\text{OH}^-] = \frac{K_3}{[\text{H}^+]} \quad (19)$$

$$[\text{HCO}_3^-] = K_2 \frac{[\text{CO}_2]}{[\text{H}^+]} \quad (20)$$

$$[\text{CO}_3^{2-}] = K_4 \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \quad (21)$$

$$[\text{R}_2\text{R}'\text{NH}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (22)$$

$$[\text{R}_2\text{R}'\text{N}] = [\text{R}_2\text{R}'\text{N}]_t - [\text{R}_2\text{R}'\text{NH}^+] \quad (23)$$

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

e	0
f	0.7514

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:

$$A [\text{H}^+]^4 + B [\text{H}^+]^3 + C [\text{H}^+]^2 + D [\text{H}^+] + E = 0 \quad (24)$$

$$A = 1$$

$$B = K_1 + [\text{R}_2\text{R}'\text{N}]_t$$

$$C = -K_2 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right) - K_3$$

$$D = -2K_2K_4 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right) - K_1K_2 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right) - K_1K_3$$

$$E = -2K_1K_2K_4 \left(\frac{P_{\text{CO}_2}}{H_{\text{CO}_2}} \right)$$

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 $[\text{H}^+]$. The CO_2 loading values were predicted using the following equation:

$$\alpha_{\text{pred}} = \frac{[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{[\text{R}_2\text{R}'\text{N}]_t} \quad (25)$$

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

$$\% \text{AARD} = \left| \frac{\alpha_{\text{pred}} - \alpha_{\text{exp}}}{\alpha_{\text{exp}}} \right| \times 100 \quad (26)$$

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.

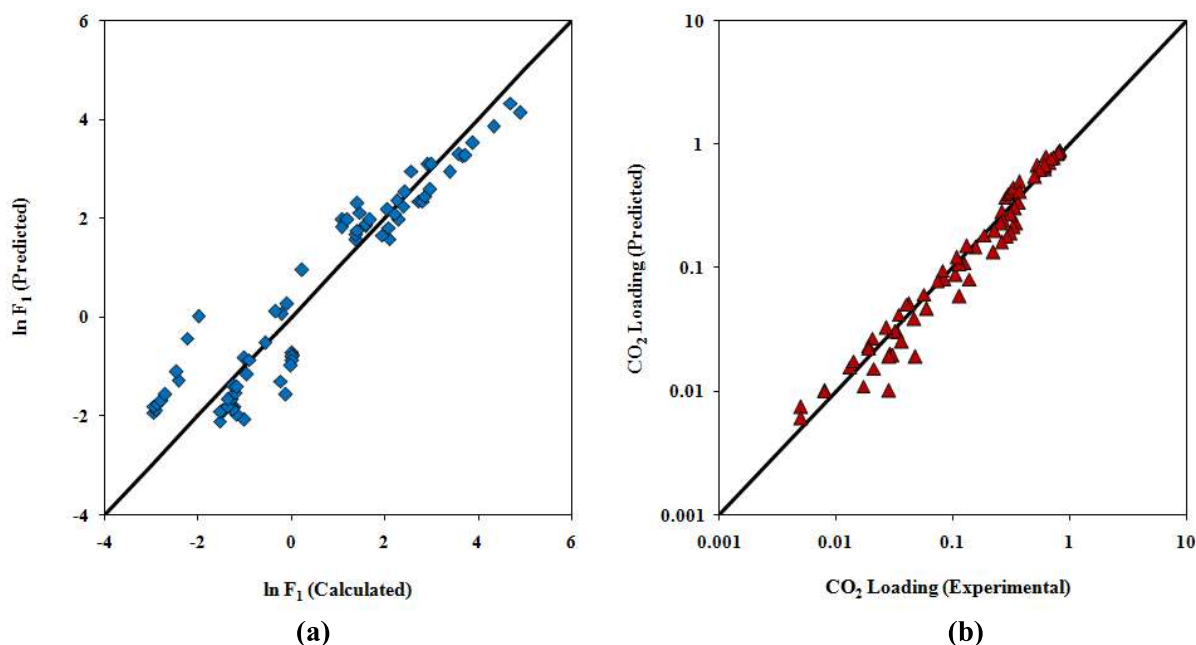


Figure 1. Parity plot for (a) Fitted parameter and (b) CO₂ Loading

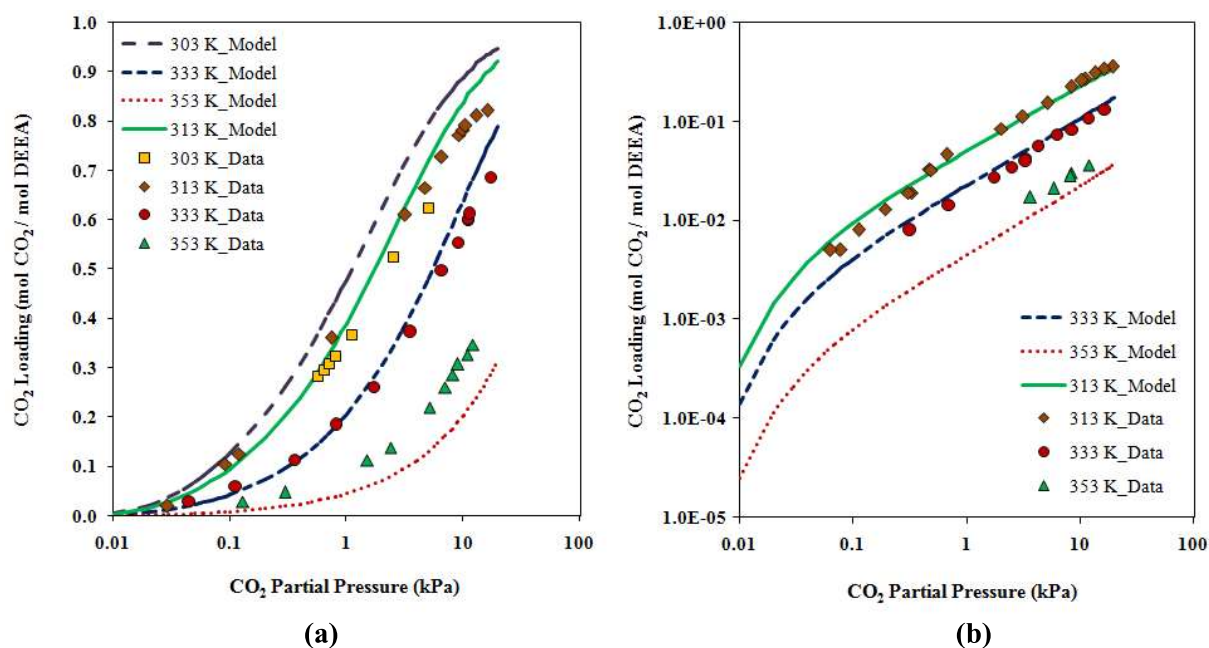


Figure 2. Equilibrium data vs. model for CO₂ solubility in aqueous solutions of (a) 2 M DEEA and (b) 5 M DEEA

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_2 increases linearly with pressure according to the Henry's law. The concentration of the carbonate and bicarbonate ions increases as more CO_2 gets absorbed into the DEEA solution, as does the concentration of DEEAH^+ 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.

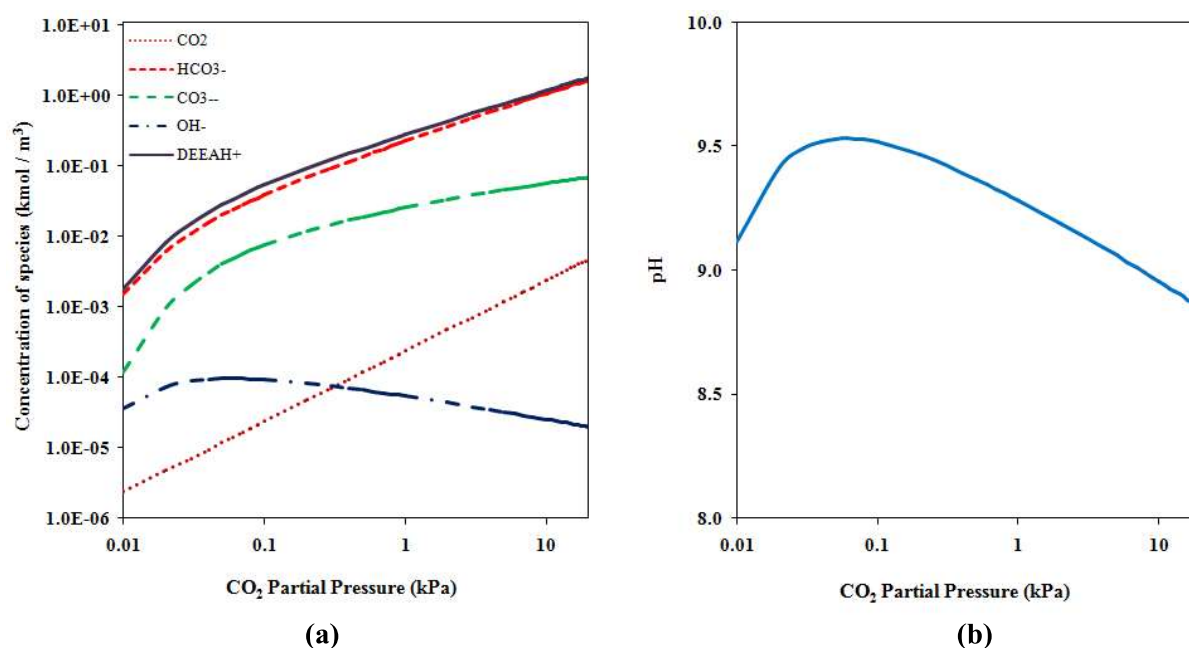


Figure 3.(a) Concentrations of different species in solution and (b) pH of solution as a function of CO_2 partial pressure in 5 M aqueous DEEA solution at 313 K

5. Conclusions

Equilibrium solubility of CO_2 in 2 M and 5 M aqueous solutions of DEEA at different temperatures and CO_2 partial pressures was modeled using the modified Kent-Eisenberg model. The model was found to predict the equilibrium behavior of CO_2 -DEEA- H_2O system quite well. AARD of 20.56% was obtained between the experimental and predicted values of CO_2 loading. Speciation data for equilibrium CO_2 absorption in 5 M DEEA solution at 313 K was also presented.

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