

GENERAL RESEARCH

Correlation and Prediction of the Solubility of Carbon Dioxide in Aqueous Alkanolamine and Mixed Alkanolamine Solutions

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The solubility of carbon dioxide in aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), MEA + AMP, and DEA + AMP was measured at 40, 60, and 80 °C. Equilibrium partial pressures of CO₂ ranged from approximately 0.1 to 50 psia. The modified Kent–Eisenberg model was used to determine the deprotonation constant and carbamate stability constant for MEA, DEA, and AMP solutions at different temperatures. The solubility of CO₂ in aqueous mixtures of AMP with MEA or DEA has been predicted using the modified Kent–Eisenberg model and reaction equilibrium constants, which were determined from each amine. The predicted values were in good agreement with the experimental data over a wide range of equilibrium CO₂ partial pressure, temperature, and solution concentration. The concentration of the liquid-phase species was calculated as a function of CO₂ loading, and some qualitative trends were obtained.

1. Introduction

Aqueous solutions of alkanolamines have been widely used in the removal processes of acid gas. Industrially important alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA). The primary and secondary amines, such as MEA or DEA, can readily react with CO₂ to form the stable carbamate, and the CO₂ loading is limited to 0.5 mol of CO₂/mol of amine by the reaction stoichiometry. Although a certain amount of carbamate hydrolysis occurs with these amines so that the CO₂ loading may be greater than 0.5, particularly at high absorption pressures, the loading of CO₂ in these amines is still less than unity. Tertiary amines such as MDEA do not form stable carbamate, thus allowing CO₂ loading to reach 1.0 mol of CO₂/mol of amine. However, the CO₂ absorption rates for tertiary amines are very low, which tends to limit their industrial importance.

Sartori and Savage reported a new class of amines, sterically hindered amines, which are capable of high loading of CO₂ because their carbamates are relatively unstable.¹ The stoichiometry of the reaction allows loading of CO₂ up to more than 1.0 mol of CO₂/mol of hindered amine. An example of the sterically hindered alkanolamines is 2-amino-2-methyl-1-propanol (AMP), which is the hindered form of MEA.

Recently, great attention has been focused on the use of amine blends to maximize the desirable qualities of the individual amines, which brings about a considerable improvement in absorption and a great savings in the energy requirement. Blends of primary and tertiary amines such as MEA and MDEA have been discussed by Campbell and Weiland² and Chakravarty et al.³

Compared to MDEA, AMP has the same CO₂ loading capacity but has a higher reaction rate constant for the reaction with CO₂. Therefore, blends of AMP/MEA or AMP/DEA may be new attractive solvents. Li and Chang⁴ and Seo and Hong⁵ reported solubility data for CO₂ in mixtures of AMP/MEA and AMP/DEA. However, more accurate solubility data, a vapor–liquid equilibrium model, and correlations for representing aqueous CO₂/alkanolamine systems are essential in calculations for process simulation and the design of the gas-treating operation.

2. Experimental Apparatus and Methods

The equipment used in the measurement of CO₂ solubility is shown in Figure 1. It consisted of an equilibrium cell for absorption and a loading cylinder for sampling. The equilibrium cell had an internal volume of about 502 cm³, and the liquid in the cell was stirred by means of a magnetic stirrer. The volume of the loading cylinder attached to the equilibrium cell was about 500 cm³. The temperature and pressure of the equilibrium cell and the loading cylinder were measured by a Pt-type thermocouple and a digital gauge (Data Instruments Co.; ranges 0–100 psia ± 0.25%, ± 0.01% °C). MEA, DEA, and AMP were obtained from Yakuri and Janssen Co. and had purity greater than 99%. They were used without further purification. The purity of CO₂ and nitrogen gas was greater than 99.9%. Prior to the experiment, aqueous solutions of alkanolamine were prepared from distilled water and about 100 cm³ of the amine solution was introduced to the equilibrium cell. The weight of the solution was measured by a digital balance (Precisa Co.; ranges 0–30 kg ± 0.1 g). The equilibrium cell was purged with nitrogen for a short time to remove the traces of air. When necessary, more nitrogen was added to maintain the system pressure above 1 atm. Because the solubility of nitrogen was

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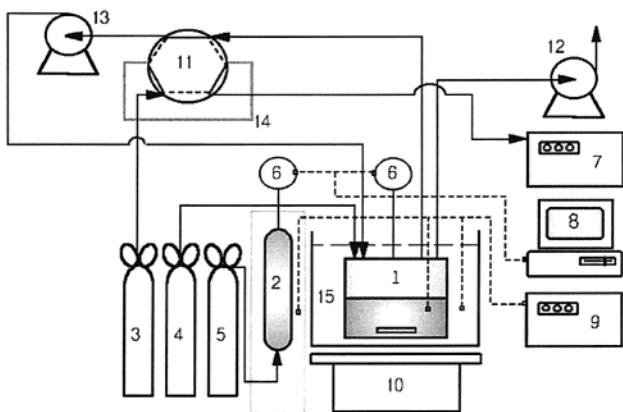


Figure 1. Schematic diagram of the experimental apparatus.

1. Reactor	2. Sample cylinder
3. He gas	4. N ₂ gas
5. CO ₂ gas	6. Pressure transducer
7. Gas chromatography	8. Data acquisition
9. Temperature controller	10. Magnetic stirrer
11. Six-way valve	12. Vacuum pump
13. Circulation pump	14. Sample loop
15. Water bath	

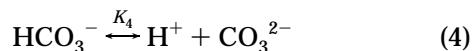
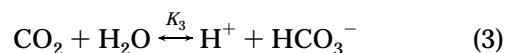
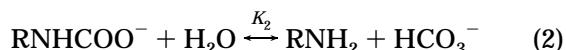
extremely small, any nitrogen effects were usually neglected. The equilibrium cell was enclosed in an electrically heated water bath maintained at $\pm 0.1^\circ\text{C}$ of the setpoint temperature. The CO₂ in the loading cylinder was introduced to the equilibrium cell through the gas inlet valve, and the pressure drop of the loading cylinder was measured. The virial equation of state was used to determine the amount of CO₂. When the pressure of the equilibrium cell did not change for 5 h, the equilibrium was assumed to have been reached. The vapor phase was circulated through the sample loop and analyzed by means of gas chromatography (Donam System Co. model DS6200 with a 6 ft long, $1/8$ in. o.d. column packed with Porapak Q). It was possible to determine the amount of CO₂ in the gas phase of the equilibrium cell by the virial equation of state and the CO₂ partial pressure of the gas phase. The moles of absorbed CO₂ is the difference between the moles of CO₂ supplied from the loading cylinder and the moles of CO₂ remaining in the gas phase of the equilibrium cell. The CO₂ loading is usually represented in terms of the moles of absorbed CO₂ per mole of amine.

3. Mathematical Relation

The first approach to correlate the solubility data for a CO₂/alkanolamine/water system was made by Mason and Dodge.⁶ However, it was only a curve-fitting approach, and the reactions between alkanolamines and CO₂ had not been studied. Danckwerts and McNeil used pseudoequilibrium constants which did not contain activity coefficients and related these constants to the ionic strength of the solution.⁷ Kent and Eisenberg developed a simple model for predicting equilibrium and neglected activity coefficients.⁸ Their model is based on several equilibrium constants and the Henry's law relationship. A more rigorous and sophisticated model was suggested by Deshmukh and Mather.⁹ Their model explicitly accounts for activity coefficients and all of the possible ionic species. However, it is very complex and requires solution of a set of nonlinear equations, which

is computationally time-consuming. Also, It is highly possible that false convergence can arise. Our equilibrium model is based on the Kent and Eisenberg model, and we assume all activity coefficients and fugacity coefficients to be unity for single- and mixed-amine systems. Although our model is relatively simple, we found that it correlates and predicts the solubility data fairly well while saving computing time. So, if computing time and the convergence problems are considered, our simple model can be used more usefully than a complex one in the actual absorption process.

3.1. Equilibrium Model I for Single-Alkanolamine Aqueous Solutions. The Kent–Eisenberg model was chosen for the base model in this work because it had given a good performance for the prediction of CO₂ solubility in alkanolamine solutions.⁸ Some modifications of the model were necessary to adapt it to the thermodynamics of CO₂/single-amine and CO₂/mixed-amine systems, in terms of equilibrium constants and balance equations. The chemical equilibrium in the systems consisting of CO₂, alkanolamines (primary or secondary), and water is governed by the following equations. Equations 1 and 2 represent the amine protonation and the carbamate hydrolysis, respectively, and R represents the alkyl group attached to the amine group. Equations 3–5 are the typical ionization reactions for aqueous systems containing CO₂.



The equilibrium constants representing the reactions in the CO₂/amine/H₂O system are given by

$$K_a = K_1 = \frac{[\text{RNH}_2][\text{H}^+]}{[\text{RNH}_3^+]} \quad (6)$$

$$K_c = \frac{1}{K_2} = \frac{[\text{RNHCOO}^-]}{[\text{RNH}_2][\text{HCO}_3^-]} \quad (7)$$

$$K_3 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (8)$$

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

$$K_5 = [\text{H}^+][\text{OH}^-] \quad (10)$$

In addition to the above equilibrium equations, overall material and charge balances must be satisfied. In these balance equations, m denotes the molarity of the alkanolamine solution and y denotes the CO₂ loading in the solution expressed as moles of chemically combined CO₂ per mole of amine.

$$m = [\text{RNH}_2] + [\text{RNHCOO}^-] + [\text{RNH}_3^+] \quad (11)$$

$$my = [\text{RNHCOO}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (12)$$

$$[\text{H}^+] + [\text{RNH}_3^+] = [\text{RNHCOO}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (13)$$

The CO_2 equilibrium partial pressure is related to the physically dissolved CO_2 concentration in the solvent by Henry's law.

$$P_{\text{CO}_2} = H_{\text{CO}_2}[\text{CO}_2] \quad (14)$$

Once the equilibrium constants are known, the free CO_2 concentration in the liquid phase can be calculated through the computational techniques. In this work, literature values of all equilibrium constants except K_a and K_c were used in the calculation as in the model of Kent and Eisenberg. These are summarized in Table 1. Although some values of K_a and K_c have been reported, they are usually applicable to some limited system conditions. Therefore, the amine deprotonation constant K_a and carbamate stability constant K_c were determined by forcing a fit with the experimental solubility data.

In this study, there were eight species of components and ions that must be solved by eight independent equations. To solve this system of nonlinear algebraic equations, initial estimates of the concentrations had to be provided. The following initial estimates were provided, and the quasi-Newton method was used. In all cases, false convergence had not arisen.

If $[\text{CO}_3^{2-}]$ is assumed to be very small, these nonlinear equations can be solved analytically to yield

$$[\text{RNHCOO}^-] = \frac{S - [S^2 - 4y(1 - y)]^{1/2}}{2} = f_{(y)} \quad (15)$$

$$[\text{RNH}_2] = m(1 - y - f_{(y)}) \quad (16)$$

$$[\text{RNH}_3^+] = my \quad (17)$$

$$[\text{HCO}_3^-] = m(y - f_{(y)}) \quad (18)$$

$$[\text{CO}_2] = \frac{K_a f_{(y)} y}{K_3 K_c [1 - y - f_{(y)}]^2} \quad (19)$$

$$[\text{H}^+] = [\text{OH}^-] = 1.0E - 8 \quad (20)$$

$$[\text{CO}_3^{2-}] = 1.0E - 4 \quad (21)$$

where

$$S = 1 + 1/K_c m \quad (22)$$

Numerical values for K_a and K_c were determined using the Levenberg–Marquardt algorithm that minimizes the difference between the measured values of equilibrium CO_2 partial pressures and the values calculated from the model. However, simple minimization of the sum of differences between measured and calculated values would weight the high partial pressure data almost to the exclusion of the low partial pressure

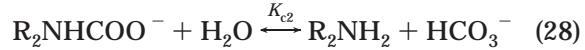
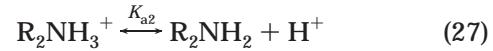
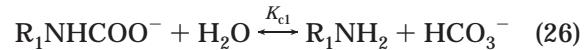
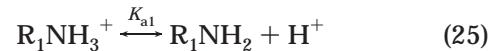
data. Therefore, the simplest unbiased objective function has the following typical term:

$$\left| \frac{\text{measured} - \text{calculated}}{\text{measured}} \right| \quad (23)$$

The objective function is the sum of the individual discrepancy functions:

$$F = \sum_i \left| \frac{(P_{\text{CO}_2})_i^{\text{exp}} - (P_{\text{CO}_2})_i^{\text{cal}}}{(P_{\text{CO}_2})_i^{\text{exp}}} \right| \quad (24)$$

3.2. Equilibrium Model II for Mixed-Alkanolamine Aqueous Solutions. Equilibrium model II for an aqueous mixture of alkanolamine solutions is analogous to equilibrium model I for single-alkanolamine aqueous solutions. Equations describing the $\text{CO}_2/\text{MEA}/\text{AMP}$ aqueous system equilibrium, with subscripts 1 and 2 representing MEA and AMP, respectively, are as follows:



The expressions for the apparent equilibrium constants are

$$K_{a1} = \frac{[\text{R}_1\text{NH}_2][\text{H}^+]}{[\text{R}_1\text{NH}_3^+]} \quad (29)$$

$$K_{c1} = \frac{[\text{R}_1\text{NHCOO}^-]}{[\text{R}_1\text{NH}_2][\text{HCO}_3^-]} \quad (30)$$

$$K_{a2} = \frac{[\text{R}_2\text{NH}_2][\text{H}^+]}{[\text{R}_2\text{NH}_3^+]} \quad (31)$$

$$K_{c2} = \frac{[\text{R}_2\text{NHCOO}^-]}{[\text{R}_2\text{NH}_2][\text{HCO}_3^-]} \quad (32)$$

The typical ionization reactions for aqueous systems containing CO_2 , which are represented by eqs 3–5, are also involved, and the following balance equations for the reacting species can be formed.

$$m_1 = [\text{R}_1\text{NH}_2] + [\text{R}_1\text{NHCOO}^-] + [\text{R}_1\text{NH}_3^+] \quad (33)$$

$$m_2 = [\text{R}_2\text{NH}_2] + [\text{R}_2\text{NHCOO}^-] + [\text{R}_2\text{NH}_3^+] \quad (34)$$

$$(m_1 + m_2)y = [\text{R}_1\text{NHCOO}^-] + [\text{R}_2\text{NHCOO}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (35)$$

$$[\text{H}^+] + [\text{R}_1\text{NH}_3^+] + [\text{R}_2\text{NH}_3^+] = [\text{R}_1\text{NHCOO}^-] + [\text{R}_2\text{NHCOO}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (36)$$

where m_1 and m_2 denote the molarity of MEA and AMP and y denotes the CO_2 loading in the solution expressed

Table 1. Equilibrium Constants and Henry's Law Constants

equilibrium constant ^a	<i>A</i>	<i>B</i> × 10 ⁻⁴	<i>C</i> × 10 ⁻⁸	<i>D</i> × 10 ⁻¹¹	<i>E</i> × 10 ⁻¹³
<i>K</i> ₃ (mol/L)	-241.818	29.8253	-1.485 28	0.332 648	-0.282 39
<i>K</i> ₄ (mol/L)	-294.74	36.4385	-1.841 58	0.415 793	-0.354 29
<i>K</i> ₅ [(mol/L) ²]	39.5554	-9.879	0.568 83	-0.146 451	0.136 146
<i>H</i> _{CO₂} (kPa·L/mol)	22.2819	-1.38306	0.069 13	-0.015 59	0.012 004

^a $K_i = \exp[A + B/T + C/T^2 + D/T^3 + E/T^4]$ and $H_{CO_2} = \exp[A + B/T + C/T^2 + D/T^3 + E/T^4]/51.71475$ for T in K.

as moles of chemically combined CO₂ per mole of amine. As in the equilibrium model I, Henry's law relates CO₂ partial pressure to the physically dissolved CO₂ concentration in the solvent according to eq 14.

For an aqueous mixed-amine solution with known concentrations m_1 , m_2 , and y , all 11 equations can be used to solve 11 unknowns: [R₁NH₂], [R₂NH₂], [R₁NHCOO⁻], [R₂NHCOO⁻], [R₁NH₃⁺], [R₂NH₃⁺], [HCO₃⁻], [CO₃²⁻], [CO₂], [H⁺], and [OH⁻]. Equilibrium constants and initial estimates of the concentration are also necessary to solve these nonlinear algebraic equations. Equilibrium constants including K_3 , K_4 , and K_5 were obtained in the literature.⁸ However, deprotonation constants K_{a1} and K_{a2} and carbamate stability constants K_{c1} and K_{c2} were obtained by the least-squares fitting to the experimental solubility data of MEA and AMP, respectively, using the equilibrium model I. The following initial estimates were provided, and the quasi-Newton method was used.

$$[R_1NH_2] = m_1(1 - y - f_{1(y)}) \quad (37)$$

$$[R_2NH_2] = m_2(1 - y - f_{2(y)}) \quad (38)$$

$$[R_1NH_3^+] = m_1y \quad (39)$$

$$[R_2NH_3^+] = m_2y \quad (40)$$

$$[R_1NHCOO^-] = \frac{S_1 - [S_1^2 - 4y(1-y)]^{1/2}}{2} = f_{1(y)} \quad (41)$$

$$[R_2NHCOO^-] = \frac{S_2 - [S_2^2 - 4y(1-y)]^{1/2}}{2} = f_{2(y)} \quad (42)$$

$$[CO_2] = \frac{K_{a1} f_{1(y)} y}{K_3 K_{c1} [1 - y - f_{1(y)}]^2} + \frac{K_{a2} f_{2(y)} y}{K_3 K_{c2} [1 - y - f_{2(y)}]^2} \quad (43)$$

$$[HCO_3^-] = (m_1 + m_2)(y - f_{1(y)} - f_{2(y)}) \quad (44)$$

$$[H^+] = [OH^-] = 1.0E-8 \quad (45)$$

$$[CO_3^{2-}] = 1.0E-3 \quad (46)$$

where

$$S_1 = 1 + 1/K_{c1}m_1 \quad (47)$$

$$S_2 = 1 + 1/K_{c2}m_2 \quad (48)$$

In all cases, false convergence had not arisen. This model is applicable to the CO₂/DEA/AMP/H₂O system

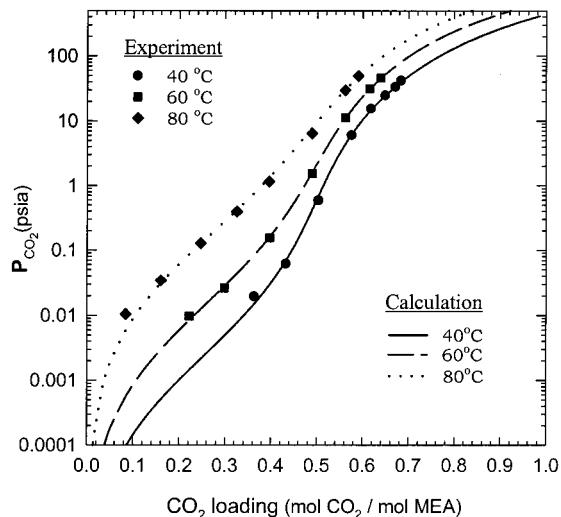


Figure 2. Solubility of CO₂ in a 30 wt % aqueous MEA solution.

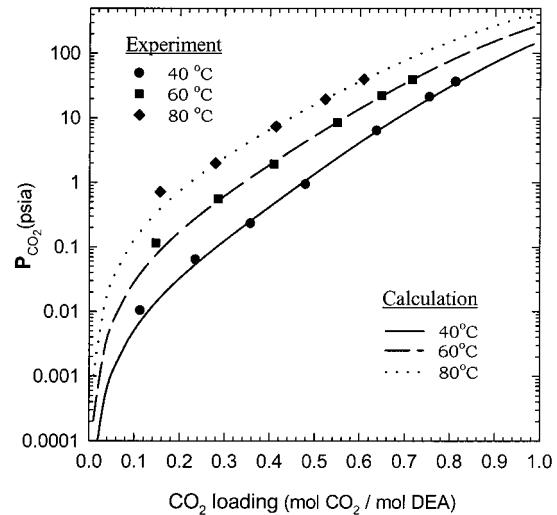


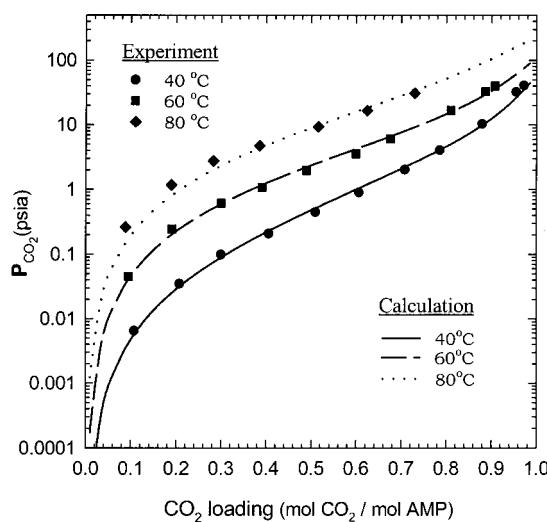
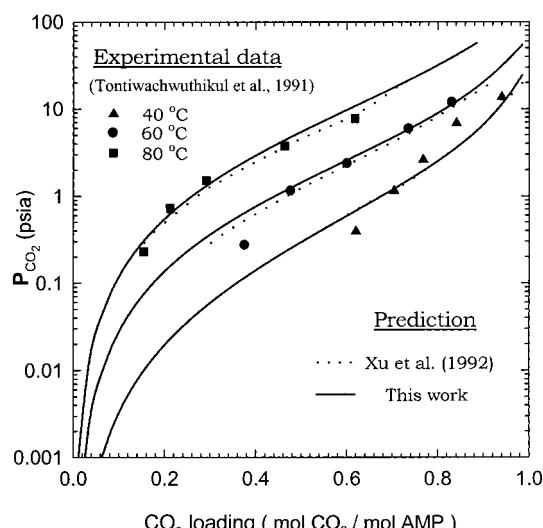
Figure 3. Solubility of CO₂ in a 30 wt % aqueous DEA solution and other primary and secondary mixed-alkanolamine solutions without any modification.

4. Results and Discussion

4.1. Determination of Equilibrium Constants from Single-Amine Data. The solubility of CO₂ in 30 wt % aqueous MEA, DEA, and AMP solutions was measured to determine the deprotonation constants (K_a) and the carbamate stability constants (K_c) for the individual amines at 40, 60, and 80 °C. The experimental results are plotted in Figures 2–4 for three aqueous amines. K_a and K_c , which were obtained by using equilibrium model I and experimental data, are listed in Table 2. The solubility curves, which were calculated from equilibrium model I, K_a , and K_c , are in good agreement with the experimental data. The average absolute percentage deviations range from 4.3% to 17.5% in the CO₂ partial pressure, and they are listed in Table 3.

Table 2. Values of K_a and K_c

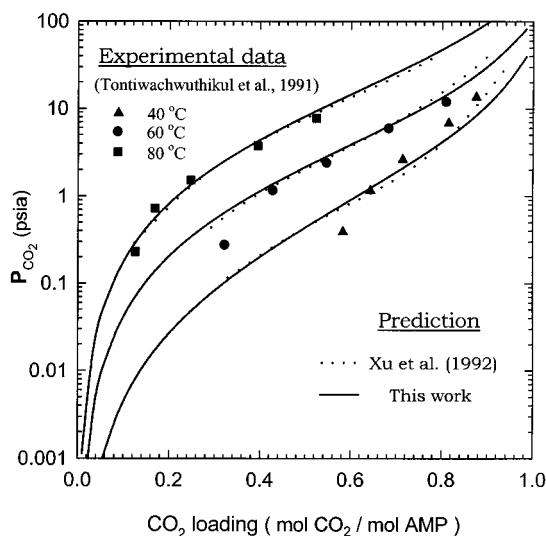
temp (°C)	MEA		DEA		AMP	
	K_a (mol/L)	K_c (L/mol)	K_a (mol/L)	K_c (L/mol)	K_a (mol/L)	K_c (L/mol)
40	2.2830×10^{-10}	26.771	8.6520×10^{-10}	2.297	2.4290×10^{-10}	0.2767
60	6.1220×10^{-10}	16.150	2.5760×10^{-9}	1.510	9.3470×10^{-10}	1.5070×10^{-4}
80	2.0350×10^{-9}	6.860	5.8750×10^{-9}	0.879	2.7020×10^{-9}	3.0250×10^{-8}

**Figure 4.** Solubility of CO_2 in a 30 wt % aqueous AMP solution.**Figure 5.** Comparison of CO_2 solubility prediction in a 2 M aqueous AMP solution.**Table 3.** Average Deviation for Correlations and Predictions of Solubility Data

system	temp (°C)	amine concn	APD (%) ^a	Figure
MEA	40	30 wt %	7.7	2
	60	30 wt %	4.3	
	80	30 wt %	14.9	
DEA	40	30 wt %	9.3	3
	60	30 wt %	6.9	
	80	30 wt %	7.2	
AMP	40	30 wt %	12.0	4
	60	30 wt %	11.4	
	80	30 wt %	17.5	
AMP (ref 12)	40	2 M	33.4 (35.5 ^b)	5
	60	2 M	30.9 (28.0 ^b)	
	80	2 M	23.3 (14.8 ^b)	
AMP (ref 12)	40	3 M	40.3 (37.7 ^b)	6
	60	3 M	38.4 (35.4 ^b)	
	80	3 M	14.9 (15.8 ^b)	
MEA/AMP	40	20 wt %/10 wt %	14.2	7
		10 wt %/20 wt %	13.9	
		5 wt %/25 wt %	11.3	
	60	20 wt %/10 wt %	14.5	8
		10 wt %/20 wt %	15.3	
	80	20 wt %/10 wt %	12.6	9
		10 wt %/20 wt %	9.4	
DEA/AMP	40	20 wt %/10 wt %	17.5	10
		10 wt %/20 wt %	10.9	
	60	20 wt %/10 wt %	8.9	11
		10 wt %/20 wt %	11.2	
	80	20 wt %/10 wt %	7.1	12
		10 wt %/20 wt %	9.4	

^a APD = $\sum_{i=1}^n |(P_{\text{CO}_2})_i^{\text{exp}} - (P_{\text{CO}_2})_i^{\text{cal}}|/(P_{\text{CO}_2})_i^{\text{exp}}$. ^bXu et al.¹³

To check the general applicability of the equilibrium model and the equilibrium constants determined in this work, the experimental data for AMP published by Tontiwachwuthikul et al.¹⁰ were compared with the predicted values provided by this model and the model of Xu et al.¹¹ Figures 5 and 6 show the comparison results for 2 and 3 M aqueous AMP solutions. The predicted values are in good agreement with the experimental data. The average percent deviations were calculated and listed in Table 3. From these results, it is noticeable that two models represent almost equal

**Figure 6.** Comparison of CO_2 solubility prediction in a 3 M aqueous AMP solution.

prediction results. The model of Xu et al. is rigorous and complex, but it is no better than our simple model.¹¹ Therefore, if the computing time and the convergence problems in the equilibrium calculation are considered, this simple model can be used more usefully in the actual absorption processes.

4.2. Prediction of CO_2 Solubility in Mixed-Amine Solutions. The solubility of CO_2 in aqueous $\text{MEA}_{(1)}$ / $\text{AMP}_{(2)}$ and $\text{DEA}_{(1)}$ / $\text{AMP}_{(2)}$ mixtures was measured at $w_1 = 0.3/w_2 = 0.0$, $w_1 = 0.2/w_2 = 0.1$, $w_1 = 0.1/w_2 = 0.2$, and $w_1 = 0.0/w_2 = 0.3$, where w is the mass fraction of the solution. The CO_2 solubility data in aqueous MEA/AMP mixed solutions are plotted in Figures 7–9. From the relative positions of the equilibrium curves, it is clear that above a certain CO_2 partial pressure, corresponding to a CO_2 loading of approximately 0.5 mol of CO_2/mol of amine, the CO_2 solubility in a 30 wt %

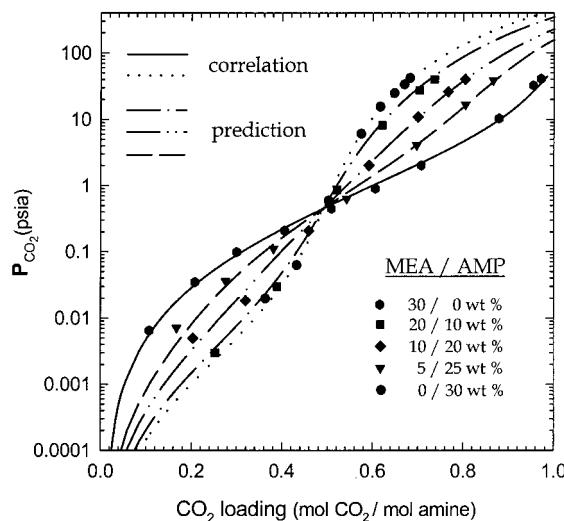


Figure 7. Solubility of CO_2 in mixed MEA/AMP solutions at 40 $^{\circ}C$ (MEA + AMP = 30 wt %).

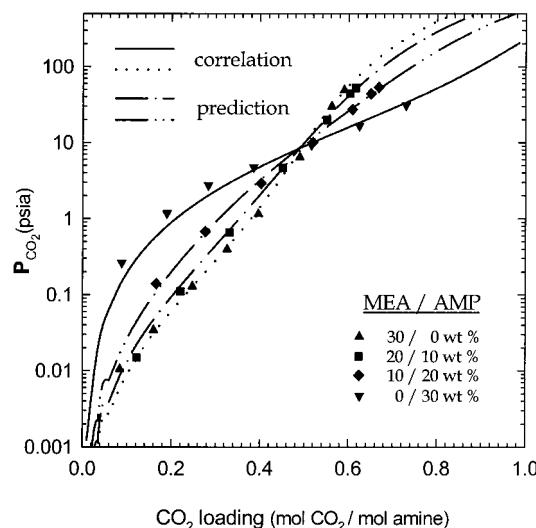


Figure 9. Solubility of CO_2 in mixed MEA/AMP solutions at 80 $^{\circ}C$ (MEA + AMP = 30 wt %).

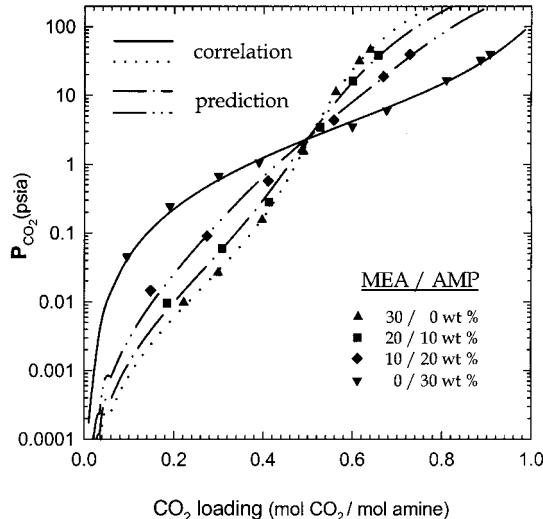


Figure 8. Solubility of CO_2 in mixed MEA/AMP solutions at 60 $^{\circ}C$ (MEA + AMP = 30 wt %).

aqueous AMP was greater than that of MEA. This is primarily due to the fact that AMP forms a very unstable carbamate upon reaction with CO_2 and requires one amine molecule for each CO_2 molecule reacted. However, the reaction of MEA with CO_2 to form very stable carbamate, which could not be converted to bicarbonate and remained in the solution, resulted in the conversion of two amine molecules for each reacted CO_2 molecule. Hence, for an aqueous solution of MEA, it is reasonable to assume that the amine would completely convert to products at CO_2 loading greater than 0.5 mol of CO_2 /mol of amine and the sudden change of equilibrium partial pressure occurred because of physical absorption rather than chemical absorption. If the solution mixture of MEA and AMP at low CO_2 loading is considered, MEA can react better than AMP with CO_2 because the reactivity of MEA to CO_2 is greater than that of AMP. However, as CO_2 loading increased, unreacted MEA decreased and resulted in an increase in the ratio of AMP to MEA. Therefore, both MEA and AMP seemed to significantly affect the solubility of CO_2 at any given partial pressure. If CO_2 loading was considerably high, the equilibrium would be closer to that of AMP than to that of MEA. By this argument, the CO_2 /MEA equilibrium curve crossed the

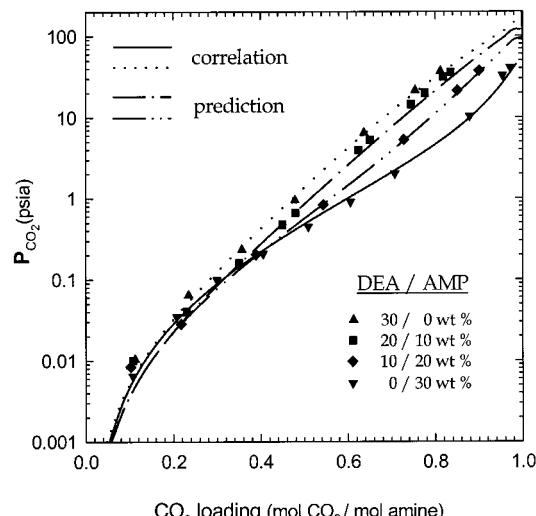


Figure 10. Solubility of CO_2 in mixed DEA/AMP solutions at 40 $^{\circ}C$ (DEA + AMP = 30 wt %).

CO_2 /AMP curve, and similar results were previously noted by Li and Chang.⁴ Figures 7–9 represent that increasing temperature resulted in increasing equilibrium pressure and the point of intersection appeared. The prediction results were obtained by equilibrium model II using the equilibrium data and the equilibrium constant K_a and K_c for individual amines at each temperature. The results are in good agreement with the experimental data. These results indicate that exact prediction is possible at any mass fraction of the mixed-amine solution. The CO_2 solubility data in aqueous DEA/AMP mixed solutions are plotted in Figures 10–12. DEA was not as reactive to CO_2 as MEA, and it represented higher equilibrium pressure than MEA at low CO_2 loading. The addition of MEA to an aqueous AMP solution resulted in the decrease of the equilibrium CO_2 partial pressure at low to moderate loading, but the addition of DEA did not. DEA nearly had the same tendency to absorb CO_2 like AMP at low loading. However, as CO_2 loading increased, DEA formed stable carbamate as in the case of MEA and the equilibrium pressure was higher than that in the case of AMP. The prediction curves represented in Figures 10–12 for mixed DEA/AMP solutions are in good agreement with

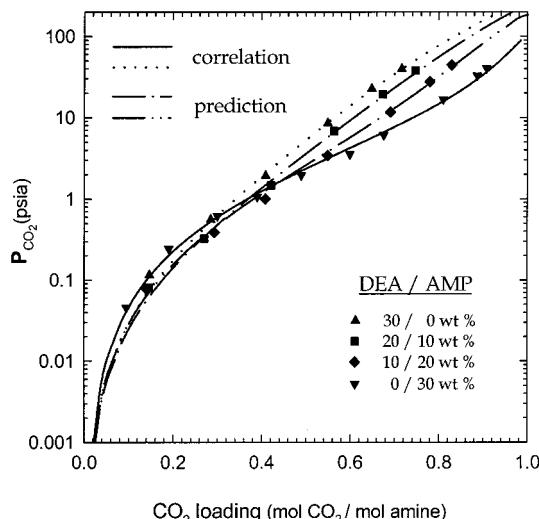


Figure 11. Solubility of CO_2 in mixed DEA/AMP solutions at 60 $^{\circ}\text{C}$ ($\text{DEA} + \text{AMP} = 30$ wt %).

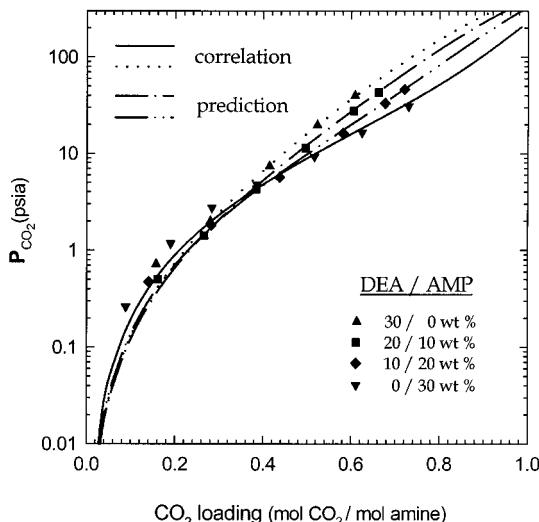


Figure 12. Solubility of CO_2 in mixed DEA/AMP solutions at 80 $^{\circ}\text{C}$ ($\text{DEA} + \text{AMP} = 30$ wt %).

the experimental data. It is clear from these results that the equilibrium model II can be used to represent the CO_2 equilibrium with mixed primary and secondary amines and it can provide good prediction results.

4.3. Liquid-Phase Concentrations of Chemical Species. The equilibrium model might be used to estimate the concentration of the liquid-phase species as a function of CO_2 loading, and some qualitative trends could be indicated. Based on this model, the concentration profiles for several significant species of components and ions were obtained as a function of the CO_2 loading in the solution. Figures 13 and 14 show equilibrium concentration profiles for a CO_2 -loaded 10 wt % MEA/20 wt % AMP mixture and a 10 wt % DEA/20 wt % AMP mixture at 40 $^{\circ}\text{C}$. In the case of the MEA and AMP mixtures shown in Figure 13, the concentration of MEA decreased rapidly at loading below 0.2 mol of CO_2 /mol of amine while the concentration of AMP decreased slowly with loading in this range. However, the degree of AMP reduction increased as the CO_2 loading increased above 0.2 mol/mol of amine. Figure 13 also indicates that MEA reacted preferentially with CO_2 and it formed a very stable carbamate. It increased at first and then decreased with increasing CO_2 loading

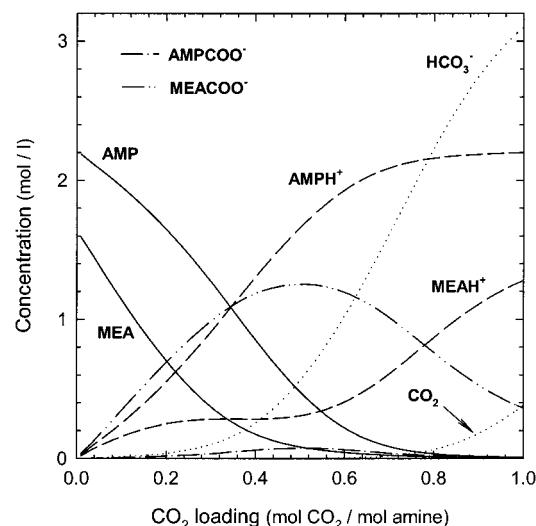


Figure 13. Liquid-phase concentration of a CO_2 -loaded 10 wt % $\text{MEA} + 20$ wt % AMP aqueous solution at 40 $^{\circ}\text{C}$.

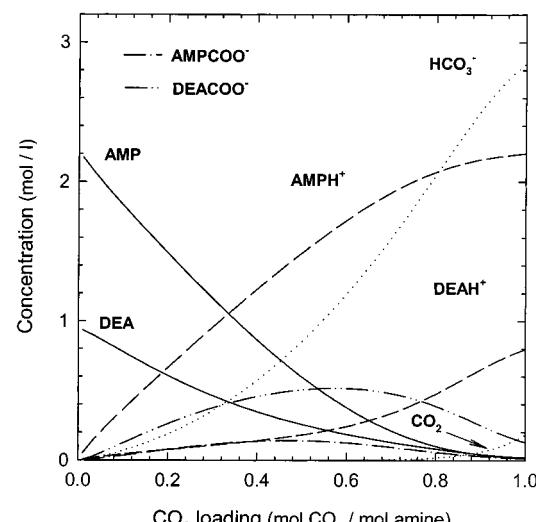


Figure 14. Liquid-phase concentration of a CO_2 -loaded 10 wt % $\text{DEA} + 20$ wt % AMP aqueous solution at 40 $^{\circ}\text{C}$.

by the carbamate hydrolysis reaction. However, even at the CO_2 loading of 1.0 mol/mol of amine, a significant fraction of CO_2 was present like the carbamate in the mixed-amine solution. Note that MEA was almost completely converted to protonated MEA or carbamate at a loading of 0.4 mol of CO_2 /mol of amine.

Figure 14 indicates that DEA disappeared at a slower rate than MEA in the mixed solutions and the carbamate of DEA was not as stable as that of MEA. For the DEA/AMP mixture, unreacted DEA was present in the solution until the CO_2 loading of 0.8 mol/mol of amine. Note that unreacted AMP decreased monotonically with increasing CO_2 loading. This means that DEA was not as reactive as MEA with CO_2 . These results suggest that while the addition of MEA affects CO_2 solubility greatly at low loading, DEA has little effect on it.

5. Conclusions

This paper presents experimental data for solubility of CO_2 in 30 wt % MEA, DEA, AMP, MEA + AMP, and $\text{DEA} + \text{AMP}$ solutions at 40, 60, and 80 $^{\circ}\text{C}$. An equilibrium model based on the Kent–Eisenberg model was presented for the prediction of the equilibrium

solubility of CO₂ in individual and mixed-alkanolamine solutions. By the experimental data and the model calculation, the equilibrium constants and the carbamate stability constants for the aqueous MEA, DEA, and AMP solutions were determined. The results predicted by the model were in good agreement with the experimental data. The concentrations of liquid-phase species were estimated as a function of CO₂ loading. This work seems to be useful for representing the vapor–liquid equilibrium of CO₂ in mixed primary and secondary alkanolamine aqueous solutions.

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Nomenclature

AMP = 2-amino-2-methyl-1-propanol
 DEA = diethanolamine
 H = Henry's law constant
 K = equilibrium constant
 m = molarity
 MDEA = methyldiethanolamine
 MEA = monoethanolamine
 P = pressure
 T = temperature
 y = loading of carbon dioxide

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