

## Prediction of Equilibrium Solubility of Carbon Dioxide in Aqueous 2-Amino-2-methyl-1,3-propanediol Solutions

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(Received 10 December 1999 • accepted 24 March 2000)

**Abstract**—The modified Kent-Eisenberg model was used to predict the solubility of carbon dioxide in aqueous 2-amino-2-methyl-1,3-propanediol (AMPD) solutions over a wide range of solvent concentration (10-30 mass %), temperature (30-60 °C), and partial pressure of carbon dioxide (5-1,100 kPa). For more accurate prediction, a new set of experimental data of this system was also presented and used in model calculation. The predicted results by the modified Kent-Eisenberg model were found to be in good agreement with the experimental data. The equilibrium constant,  $K_1$ , which represented the deprotonation reaction of AMPD, was expressed as a function of not only temperature but also loading capacity and amine concentration.

Key words: Absorption, Carbon Dioxide, AMPD, Solubility, Kent-Eisenberg Model

### INTRODUCTION

One of the most promising processes to remove a large amount of carbon dioxide from gas mixtures such as flue gas streams of thermal power plants is absorption by aqueous alkanolamine solutions. The solubility data of gases in absorbent and the model predicting the solubility are essential for the process simulation and design of absorbers and regenerators.

Industrially important chemical absorbents used to remove carbon dioxide are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA). Aqueous MEA solutions are the most frequently used alkanolamine absorbents due to their high reactivity with carbon dioxide, low solvent cost, and ease of reclamation [Isaacs et al., 1980]. It is also known, however, that aqueous MEA solutions are corrosive and require high regeneration energy. Aqueous MDEA solutions are better than MEA or DEA solutions in that they have the properties of high loading capacity (mol of CO<sub>2</sub>/mol of amine) up to 1.0, less regeneration energy, and high resistance to thermal and chemical degradation. However, the slow reactivity with carbon dioxide of MDEA solutions limits their use. Recently, sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-piperidineethanol (PE) have been proposed as new absorbents because of their advantages in loading capacity, absorption rate, and regeneration energy [Satori and Savage, 1983; Yih and Shen, 1988]. Because of the hindrance of the bulky group attached to the tertiary carbon atom, unstable carbamate ions are formed in the reaction of the AMP solutions with carbon dioxide, resulting in the theoretical loading capacity up to 1.0. A number of research papers related to the solubility of carbon dioxide in aqueous AMP solutions and blended amine solutions containing AMP have been published [Li and Chang, 1994; Seo and Hong, 1996; Tontiwachwuthikul et al., 1991]. There were several

models predicting the solubility of carbon dioxide in aqueous alkanolamine solutions. Kent and Eisenberg [1976] proposed a model predicting the solubility of carbon dioxide in the aqueous MEA and DEA solutions. They calculated the equilibrium constants for reactions involving amines only as a function of temperature by fitting to the experimental solubility data. However, the equilibrium constants are also influenced by acid gas partial pressure, acid-gas loading and amine concentration [Chakma and Meisen, 1987; Jou et al., 1982]. Hu and Chakma [1990] modified the Kent-Eisenberg model by considering these factors. Li and Shen [1993] used CO<sub>2</sub> loadings instead of CO<sub>2</sub> partial pressure in the modified Kent-Eisenberg model. Deshmukh and Mather [1981] and Austgen et al. [1991] proposed more rigorous models with activity coefficient to calculate the equilibrium constants. In spite of their complexity of calculation, the predictions of rigorous models were no better than those of the Kent-Eisenberg model [Hu and Chakma, 1990].

In our previous work [Baek and Yoon, 1998], the equilibrium solubility of carbon dioxide in aqueous 2-amino-2-methyl-1,3-propanediol (AMPD) solutions was measured at 30 °C and the concentration of 10 mass % AMPD and at 30, 40, and 60 °C and the concentration of 30 mass % AMPD. In this study, we would like to present the supplementary data set of this system and examine the applicability of the modified Kent-Eisenberg model for the prediction of the solubility behavior of carbon dioxide in aqueous alkanolamine solutions. This result may provide the thermodynamic basis required for design and operation of the gas sweetening process.

### EXPERIMENTAL

The solubilities were measured with the same apparatus, method and procedure used in our previous work [Baek and Yoon, 1998]. The equilibrium solubility of CO<sub>2</sub> in aqueous AMPD solutions was measured by using an equilibrium cell made of 316 stainless steel. When the system pressure was not changed dur-

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ing 3 h, the system was considered to be in equilibrium. The system pressure was measured by a bourdon tube type of pressure gauge (Heise, CMM-123928). The composition of the vapor phase was determined by a gas chromatograph (Hewlett-Packard, 5890 Series II Plus). At equilibrium, about 20 mL liquid sample was withdrawn at least twice from the equilibrium cell, and the loading of CO<sub>2</sub> in the aqueous absorbents was obtained by analyzing the sample by the titration method [Li and Chang, 1994]. The partial pressure of CO<sub>2</sub> was corrected for water vapor pressure at the equilibrium temperature. Aqueous AMPD solutions were prepared from deionized water and 99+% AMPD from Sigma. The CO<sub>2</sub> and N<sub>2</sub> with a purity of 99.99% were supplied from the commercial cylinders.

### MATHEMATICAL MODELLING

The equations describing the equilibrium of carbon dioxide with aqueous AMPD solutions are assumed as follows:



For these reactions, the apparent equilibrium constants are expressed as follows:

$$K_1 = [\text{H}^+][\text{RNH}_2]/[\text{RNH}_3^+] \quad (5)$$

$$K_3 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \quad (6)$$

$$K_4 = [\text{H}^+][\text{OH}^-] \quad (7)$$

$$K_5 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (8)$$

The overall material and charge balance equations are written as:

$$[\text{AMPD}] = [\text{RNH}_2] + [\text{RNH}_3^+] \quad (9)$$

$$[\text{AMPD}]\alpha = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (10)$$

$$[\text{RNH}_3^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (11)$$

where  $\alpha$  is loading capacity, which means the total number of moles of CO<sub>2</sub> absorbed in one mole of AMPD.

The physical solubility of carbon dioxide in absorbents to the partial pressure of carbon dioxide is related by Henry's law:

$$P_{\text{CO}_2} = H_{\text{CO}_2} [\text{CO}_2] \quad (12)$$

From Eqs. (5)-(11), concentrations of seven species (i.e., [RNH<sub>2</sub>], [H<sup>+</sup>], [RNH<sub>3</sub><sup>+</sup>], [HCO<sub>3</sub><sup>-</sup>], [CO<sub>2</sub>], [OH<sup>-</sup>], [CO<sub>3</sub><sup>2-</sup>]) and K<sub>1</sub> are found for known values of [AMPD],  $\alpha$ , P<sub>CO<sub>2</sub></sub>, H<sub>CO<sub>2</sub></sub>, K<sub>3</sub>, K<sub>4</sub> and K<sub>5</sub>. The equilibrium constants of Eqs. (2)-(4) and Henry's law constant are calculated from the correlations given in the literature [Kent and Eisenberg, 1976].

$$K_3 = \exp(-241.818 + 298.253 \times 10^3/T - 148.528 \times 10^6/T^2 + 332.648 \times 10^8/T^3 - 282.394 \times 10^{10}/T^4) \quad (13)$$

$$K_4 = \exp(3.5554 - 987.9 \times 10^3/T + 568.828 \times 10^7/T^2 - 146.451 \times 10^9/T^3 + 136.146 \times 10^{10}/T^4) \quad (14)$$

$$K_5 = \exp(-294.74 + 364.385 \times 10^3/T - 184.158 \times 10^7/T^2 + 415.793 \times 10^9/T^3 - 354.291 \times 10^{10}/T^4) \quad (15)$$

$$H_{\text{CO}_2} = \exp(22.2819 - 138.306 \times 10^3/T + 691.346 \times 10^6/T^2 - 155.895 \times 10^7/T^3 + 120.037 \times 10^9/T^4) / 7.50061 \quad (16)$$

The apparent equilibrium constant, K<sub>1</sub>, of Eq. (1) representing amine reaction is assumed to be a function of temperature, amine concentration and CO<sub>2</sub> loading as in the method of Li and Shen [1993].

$$K_1 = \exp(a_1 + a_2/T + a_3/T^2 + b_1\alpha + b_2\alpha^2 + b_3\alpha^3 + b_4 \ln m) \quad (17)$$

where m is AMPD concentration in molarity. The constants, a, and b<sub>i</sub>, in Eq. (17) are determined by a least-squares fit to the experimental solubility data. Using these parameters, the solubility of CO<sub>2</sub> in aqueous AMPD solutions can be calculated by solving the above nonlinear equations by Muller's method.

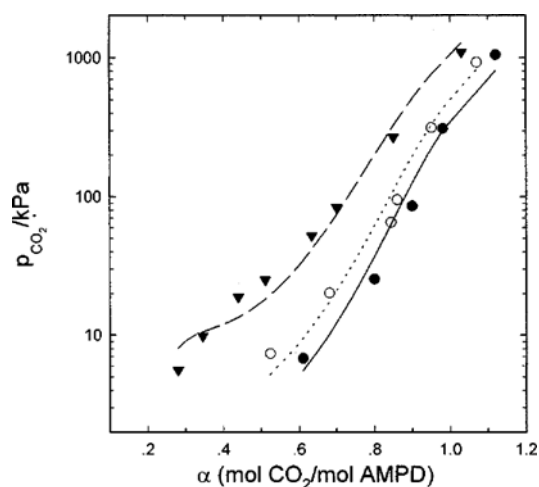
### RESULTS AND DISCUSSION

The solubility of carbon dioxide in aqueous AMPD solutions at various conditions (temperature, 30, 40, and 60 °C; concentration, 10 and 30 mass %; CO<sub>2</sub> partial pressure, 5-1,100 kPa) is presented in Table 1 and depicted in Figs. 1 and 2. As shown in Figs. 1 and 2, the solubility of carbon dioxide increases with an increase in the partial pressure of carbon dioxide, while it decreases with an increase in the system temperature. Further, it is also found that the loading capacity of CO<sub>2</sub> in the 10 mass % AMPD aqueous solution is always higher than that in the 30 mass % AMPD aqueous solution over all the temperature and pressure conditions considered. In general, these results can be easily observed for the

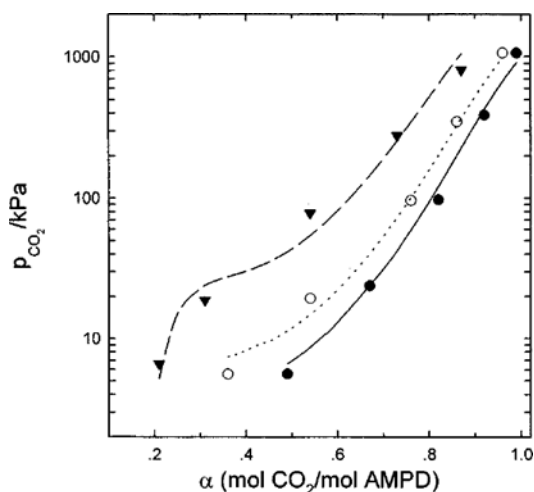
**Table 1. Solubility of CO<sub>2</sub> in aqueous AMPD solutions**

T (°C)	10 mass %		30 mass %	
	P <sub>CO<sub>2</sub></sub> /kPa	$\alpha$	P <sub>CO<sub>2</sub></sub> /kPa	$\alpha$
30	6.81	0.609	5.59	0.492 <sup>a</sup>
	25.4	0.804	23.8	0.669 <sup>a</sup>
	85.8	0.904	97.3	0.823 <sup>a</sup>
	311	0.976	389	0.920 <sup>a</sup>
	1046	1.122	1065	0.987 <sup>a</sup>
40	7.37	0.523 <sup>a</sup>	5.57	0.362 <sup>a</sup>
	20.2	0.680	19.3	0.540 <sup>a</sup>
	65.5	0.844 <sup>a</sup>	96.2	0.756 <sup>a</sup>
	95.0	0.856	349	0.859 <sup>a</sup>
	314	0.945 <sup>a</sup>	1064	0.964 <sup>a</sup>
60	927	1.069 <sup>a</sup>		
	5.61	0.280	6.59	0.206 <sup>a</sup>
	9.84	0.345	18.9	0.313 <sup>a</sup>
	18.8	0.439	78.0	0.538 <sup>a</sup>
	25.0	0.507	277	0.732 <sup>a</sup>
	52.3	0.634	807	0.865 <sup>a</sup>
	83.9	0.700		
	269	0.851		
	1097	1.027		

<sup>a</sup>Data reported in the literature [Baek and Yoon, 1998].



**Fig. 1.** Comparison of calculated and experimental results of solubility of CO<sub>2</sub> in 10 mass % aqueous AMPD solutions: ●, 30 °C; ○, 40 °C; ▼, 60 °C. Lines are calculated by the modified Kent-Eisenberg model.



**Fig. 2.** Comparison of calculated and experimental results of solubility of CO<sub>2</sub> in 30 mass % aqueous AMPD solutions: ●, 30 °C; ○, 40 °C; ▼, 60 °C. Lines are calculated by the modified Kent-Eisenberg model.

measurement of the solubility of CO<sub>2</sub> in aqueous alkanolamine solutions. The equilibrium constant,  $K_1$ , is determined by the method as suggested by Tontiwachwuthikul et al. [1991] using the solubility data in Table 1. Thus, the equilibrium constant expression is as follows:

$$K_1 = \exp(5.45131 - 1.7748 \times 10^4/T + 4.2572 \times 10^6/T^2 + 13.22769\alpha + 6.68747/\alpha - 0.78018/\alpha^2 - 0.16073 \ln m) \quad (18)$$

In Figs. 1 and 2, the predicted results by the modified Kent-Eisenberg model are compared with the experimental solubility data. The predicted partial pressures of carbon dioxide in aqueous AMPD solutions are found to be in good agreement with the experimental data over the temperature and concentration ranges considered in this work. A dramatic increase of both the experimental and predicted partial pressures of CO<sub>2</sub> in the range of high

temperature and low loading capacity was observed. Similar phenomena can be also found in the results of Li and Chang [1994] who used the modified Kent-Eisenberg model to predict the solubilities of CO<sub>2</sub> in the aqueous mixtures of MEA and AMP. For more accurate prediction, it is necessary to accumulate a great number of experimental data and to develop a theoretically correct model.

#### ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Korea Electric Power Corporation.

#### NOMENCLATURE

- $a_i, b_i$  : constants in Eq. (17)  
 $H_{CO_2}$  : Henry's law constant of carbon dioxide [kPa · m<sup>3</sup>/kmol]  
 $K_i$  : equilibrium constant defined in Eqs. (1)-(4)  
 $m$  : molarity of AMPD in aqueous solutions  
 $P_{CO_2}$  : partial pressure of carbon dioxide [kPa]  
 $RNH_2$  : represented AMPD  
 $T$  : absolute temperature [K]  
 $\alpha$  : CO<sub>2</sub> loading capacity (mol of CO<sub>2</sub>/mol of AMPD)

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