Correlation and Prediction of Solubility of CO_2 in Amine Aqueous Solutions

Goharrokhi, Mahdi

Department of Chemical Engineering, Science & Research Campus, Islamic Azad University,
Tehran, I.R. IRAN

Taghikhani, Vahid*[+]; Ghotbi, Cirous; Safekordi, Ali Akbar

Faculty of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. IRAN

Najibi, Hesam

Department of Gas Engineering, Petrology University of Technology, Ahwaz, I.R. IRAN

ABSTRACT: *The solubility of CO_2 in the primary, secondary, tertiary and sterically hindered amine aqueous solutions at various conditions was studied. In the present work, the Modified Kent-Eisenberg (M-KE), the Extended Debye-Hückel (E-DH) and the Pitzer models were employed to study the solubility of CO_2 in amine aqueous solutions. Two explicit equations are presented to evaluate the concentration of H^+ as well as the equilibrium constants of protonation reactions for the tertiary and sterically hindered amine aqueous solutions. Using the M-KE model, the equilibrium constants of protonation reactions of amines were correlated in terms of temperature, CO_2 partial pressure and amine concentration. Also the E-DH and Pitzer models were used to correlate the solubility of CO_2 in MDEA aqueous solution. The binary interaction parameters for the models studied in this work as well as the parameters for the equilibrium constants of protonation reactions were obtained using the Davidon-Fletcher-Powell (DFP) minimization method. The results show that the M-KE, E-DH and the Pitzer models can accurately predict the corresponding experimental data. Although the solubility data for CO_2 in amine aqueous solutions have been reported in the literature to a large extent, accurate data are required to model the CO_2 absorption process. Therefore, two criteria for the tertiary and sterically hindered amines were presented using the M-KE model to screen the experimental data.*

KEY WORDS: *Acid gases, Amines, CO_2 solubility, Modified kent-eisenberg model, Extended Debye-Hückel model, Pitzer model, Davidon-Fletchel-Powell minimization method.*

INTRODUCTION

Separation of acid gases, CO_2 and H_2S, from gas mixtures is one of the most important tasks in petroleum refining, natural gas processing and petrochemical industries. Although various methods have been proposed

for such processes, the gas absorption method with different solvents is the most widely used. In the acid gas absorption process the capacity and the rate of absorption of acid gases are of central importance. While the CO_2 absorption rate of the primary and secondary amines such as MEA and DEA is high, in the case of tertiary amines such as TEA and MDEA, the CO_2 absorption rate is considerably lower. Thanks to low carbamate stability, the CO_2 absorption capacity of the tertiary amine aqueous solutions is high and due to the formation of stable carbamate, the primary and secondary amines have low capacity of CO_2 absorption [1].

Sterically hindered amines such as 2-Amino-2-Methyl-1-Propanol (AMP) could be a primary amine in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to secondary or tertiary carbon atoms [2]. These amines have high capacity absorption and absorption rate as well as selectivity and degradation resistance.

Since equilibrium data are indispensable for design of gas absorption units, many researchers have reported the solubility of acid gases in various types of amines. Solubility of CO_2 in MEA, DEA and MDEA aqueous solutions at various temperatures, amine concentrations and pressures has been reported [3-14]. *Jane et al.* [15] determined the solubility of CO_2, H_2S and their mixtures in the system of DEA+AMP aqueous solution. *Teng et al.* [16] measured the solubility of acid gases in AMP at 50°C and 3.43 kmol/m³ AMP. *Roberts et al.* [17] reported the solubility of acid gases in AMP. *Tontwachwul et al.* [18] measured the solubility of CO_2 in AMP at various temperatures and AMP concentrations. They also correlated the data with the M-KE model and reported a relation to calculate the equilibrium constant of the protonation reaction.

A number of models such as Kent-Eisenberg (KE), Modified Kent-Eisenberg (M-KE), Electrolyte-NRTL, Extended Debye-Hückel (E-DH), Pitzer and Li-Mather models were proposed to correlate the solubility data. *Kent & Eisenberg* [19] modeled the solubility of acid gases and their mixtures in MEA and DEA aqueous solutions. They considered equilibrium constants of carbamate formation and protonation of these amines to be temperature-dependent only. Since the KE model is an empirical model, in a wide range of temperature, pressure and amine concentrations it cannot properly predict the solubility of acid gases in amine aqueous solutions. Although the KE equilibrium constant of carbamate formation was used in this work, the new correlations for MEA and DEA equilibrium constant of protonation reaction were presented.

To increase the accuracy of predicting the solubility of acid gases in amines, the activity coefficients must be considered. To do so, *Deshmukh et al.* [20] and *Pitzer* [21,22] proposed the E-DH and Pitzer models, respectively. It should be noted that application of these models would be more complicated than that of the K-E and M-KE. In the Pitzer, E-DH and Li-Mather models the activity coefficients were expressed in terms of long as well as short-range intermolecular forces. To consider the deviation of gas phase from the ideal gas state, the Virial, PR or SRK equations of state (EOS) can be used to calculate the fugacity coefficients of components in the gas phase [23-25].

In the M-KE model the equilibrium constant of amine protonation, $pK_1 = -\log(K_1)$ should be expressed as a function of temperature, loading or partial pressure of acid gas and amine concentration. Since loading may be directly calculated from temperature and CO_2 partial pressures, *Chakma et al.* [26] suggested using CO_2 partial pressure instead of loading in pK_1 correlations.

Jou et al. [12] used the M-KE model to correlate the experimental data and showed the dependency of pK_1 on temperature, acid gas partial pressure and amine concentration. *Chakma et al.* [26] measured the solubility of CO_2 in MDEA and BHEP aqueous solutions and correlated their own experimental data as well as those reported by *Jou et al.* [12] with the M-KE model and expressed pK_1 as a function of temperature, CO_2 and MDEA concentrations. Notably, Chakma's correlation led to inappropriate results compared to the corresponding experimental data. Therefore, the relation has not enough accuracy to predict acid gas solubility.

In this work, the amine-CO_2-H_2O systems at various temperatures and amine concentrations using the M-KE model were studied. To predict the solubility of CO_2 in various types of amine aqueous solutions, new correlations for equilibrium constants of protonation reactions are also presented in terms of temperature, CO_2 partial pressure and amine concentration. The E-DH and Pitzer models are also used to study the solubility of CO_2

in MDEA aqueous solution and the binary interaction parameters of these models are reported.
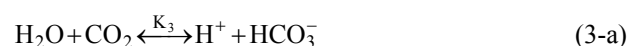
THEORETTICAL SECTION
Theory

To model solubility and calculate the equilibrium constant of the amine protonation reaction using the M-KE model, the following sets of chemical reactions for the systems of amines-CO_2-H_2O should be taken into account:

$$RR'R''NH^+ \xleftrightarrow{K_1} H^+ + RR'R''N \qquad (1\text{-}a)$$

$$K_1 = \frac{m_{H^+} m_{RR'R''N}}{m_{RR'R''NH^+}}$$

$$RR'NCOO^- + H_2O \xleftrightarrow{K_2} HCO_3^- + RR'NH \qquad (2\text{-}a)$$

$$K_2 = \frac{m_{RR'NH} m_{HCO_3^-}}{m_{RR'NCOO^-}}$$

$$H_2O + CO_2 \xleftrightarrow{K_3} H^+ + HCO_3^- \qquad (3\text{-}a)$$

$$K_3 = \frac{m_{H^+} m_{HCO_3^-}}{m_{CO_2}}$$

$$H_2O \xleftrightarrow{K_4} H^+ + OH^- \qquad (4\text{-}a)$$

$$K_4 = m_{H^+} m_{OH^-}$$

$$HCO_3^- \xleftrightarrow{K_5} H^+ + CO_3^{2-} \qquad (5\text{-}a)$$

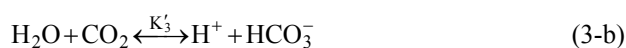$$K_5 = \frac{m_{H^+} m_{CO_3^{2-}}}{m_{HCO_3^-}}$$

Where K_i (i=1 to 5) is the equilibrium constant of the above chemical reactions. It should be stated that in order to model solubility using various activity coefficient models, the following chemical equilibrium reactions for the systems of amines-CO_2-H_2O should also be considered:

$$RR'R''NH^+ \xleftrightarrow{K_1'} H^+ + RR'R''N \qquad (1\text{-}b)$$

$$K_1' = \frac{m_{H^+} \gamma_{H^+} m_{RR'R''N} \gamma_{RR'R''N}}{m_{RR'R''NH^+} \gamma_{RR'R''NH^+}}$$
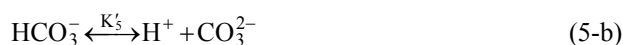
$$RR'NCOO^- + H_2O \xleftrightarrow{K_2'} HCO_3^- + RR'NH \qquad (2\text{-}b)$$

$$K_2' = \frac{m_{RR'NH} \gamma_{RR'NH} m_{HCO_3^-} \gamma_{HCO_3^-}}{m_{RR'NCOO^-} \gamma_{RR'NCOO^-} a_w}$$

$$H_2O + CO_2 \xleftrightarrow{K_3'} H^+ + HCO_3^- \qquad (3\text{-}b)$$

$$K_3' = \frac{m_{H^+} \gamma_{H^+} m_{HCO_3^-} \gamma_{HCO_3^-}}{m_{CO_2} \gamma_{CO_2} a_w}$$

$$H_2O \xleftrightarrow{K_4'} H^+ + OH^- \qquad (4\text{-}b)$$

$$K_4' = \frac{m_{H^+} \gamma_{H^+} m_{OH^-} \gamma_{OH^-}}{a_w}$$

$$HCO_3^- \xleftrightarrow{K_5'} H^+ + CO_3^{2-} \qquad (5\text{-}b)$$

$$K_5' = \frac{m_{H^+} \gamma_{H^+} m_{CO_3^{2-}} \gamma_{CO_3^{2-}}}{m_{HCO_3^-} \gamma_{HCO_3^-}}$$

It is worth stressing that the carbamate ion does not appear at all in the tertiary amine aqueous solutions and the stability of the carbamate ion in the satirically-hindered amine aqueous solutions is low enough to easily convert to amine and bicarbonate [27]. Therefore, in these solutions bicarbonate and carbonate ions are the only major chemical sinks for CO_2 and, in turn, the reactions (2-a) and (2-b) can be safely ignored [28].

Atom and charge balances in the tertiary and sterically-hindered amine aqueous solutions can be expressed by the following equations which must also be considered in addition to the chemical equilibrium equations:

$$M_{RR'R''N} + m_{RR'R''NH}^+ = m_{AMINE} \qquad (6)$$

$$m_{HCO_3^-} + m_{CO_2} + m_{CO_3^{2-}} = \alpha m_{AMINE} \qquad (7)$$

$$m_{RR'R''NH^+} + m_{H^+} = m_{HCO_3^-} + m_{OH^-} + 2m_{CO_3^{2-}} \qquad (8)$$

Where α is CO_2 loading of the amine solutions and m_{AMINE} is total amine concentration.

When using the M-KE model the following equation can be employed to evaluate the partial pressure of CO_2:

$$P_{CO_2} = H_{CO_2} m_{CO_2} \qquad (9)$$

Where H_{CO2} is Henry's constant for solubility of CO_2 in an amine aqueous solution.

In the case of the E-DH and Pitzer models, the following equation can be used to estimate the partial pressure of CO_2

$$\phi_{CO_2} P_{CO_2} = H'_{CO_2} m_{CO_2} \gamma_{CO_2} \qquad (10)$$

113

The expressions for the equilibrium and Henry's constants for CO_2 as a function of temperature used in the M-KE, E-DH and Pitzer models are presented in Tables 1 and 2. The fugacity coefficient of CO_2 was obtained using the PR equation of state [24].

Although an arbitrary activity coefficient model can be used, the E-DH and the Pitzer models were used to model the solubility of CO_2 in aqueous MDEA solutions.

The E-DH activity coefficient model can be expressed according to the following equation [20]:

$$Ln\gamma_i = \frac{-A_\phi Z_i^2 I^{.5}}{1+1.2I^{05}} + 2\sum_{\substack{j=1 \\ j\neq w}}^{nc} \beta_{ij}m_j \qquad (11)$$

Also the Pitzer activity coefficient model can be written as [29]:

$$Ln\gamma_i = -A_\phi Z_i^2 \left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}Ln\left(1+1.2\sqrt{I}\right)\right] + \qquad (12)$$

$$2\sum_{J\neq w} m_j \left\{ \beta_{ij}^{(0)} + \beta_{ij}^{(0)}\left[\frac{1-\left(1+2\sqrt{I}\right)\exp(-2\sqrt{I})}{2I}\right]\right\} -$$

$$Z_i^2 \sum_{j\neq w}\sum_{k\neq w} m_j m_k \beta_{i,j}^{(1)}\left[\frac{\left(1+2\sqrt{I}+2I\right)\exp(-2\sqrt{I})}{4I^2}\right]$$

According to the E-DH model while the activity of water is considered to be equal to the corresponding mole fraction [20], it can be straightforwardly calculated using the following equation obtained based on the Gibbs-Duhem relation from the Pitzer model:

$$Lna_w = \qquad (13)$$

$$M_w \left\{ \frac{2A_\phi I^{1.5}}{1+1.2\sqrt{I}} - 2\sum_{i\neq w}\sum_{j\neq w} m_i m_j \left[\beta_{ij}^{(0)} + \beta_{ij}^{(1)}\exp(-2\sqrt{I})\right]\right\} - M_w\sum_{i\neq w} m_i$$

Where A_ϕ and I in the above equations are the Debye - Hückel constant and ionic strength, respectively. The Debye - Hückel constant can be considered to be temperature dependent according to the following relation [30]:

$$A_\phi = -1.306568 + 0.01328238T - \qquad (14)$$
$$0.3550803\,E-4T^2 + 0.3381968E-7T^3$$

Also the molality based ionic strength of solution can be written as:

$$I = \frac{1}{2}\sum_{i=1}^{nc} m_i Z_i^2 \qquad (15)$$

In the following section, the M-KE model and the activity coefficients models will be used to study the CO_2 solubility in amine aqueous solutions.

The M-KE model

Combining Eqs. (1-a) to (5-a), concentrations of all ions and molecules in the tertiary and sterically hindered amine aqueous solutions can be directly related to the molality of H^+. From here on x stands for molality of H^+:

$$m_{RR'R''N} = \frac{m_{AMINE}K_1}{K_1 + x} \qquad (16)$$

$$m_{RR'R''NH^+} = \frac{m_{AMINE}x}{K_1 + x} \qquad (17)$$

$$m_{CO_3^{2-}} = \frac{P_{CO_2}K_3K_5}{H_{CO_2}x^2} = \frac{m_{AMINE}\alpha K_3 K_5}{x^2 + K_3 x + K_3 K_5} \qquad (18)$$

$$m_{HCO_3^-} = \frac{P_{CO_2}K_3}{H_{CO_2}x} = \frac{m_{AMINE}\alpha K_3 x}{x^2 + K_3 x + K_3 K_5} \qquad (19)$$

$$m_{OH^-} = \frac{K_4}{x} \qquad (20)$$

The partial pressure of CO_2 can be expressed by the following relation:

$$P_{CO_2} = \frac{m_{AMINE}\alpha H_{CO_2}x^2}{x^2 + K_3 x + K_3 K_5}$$

Looking at Eqs. (16)-(20) reveals that to calculate the concentrations of all ions and molecules present in the tertiary and sterically-hindered amine aqueous solutions, the H^+ concentration should be determined. Therefore, Eqs. (9), (18) and (19) are combined with Eq. (7) to determine x. Such combination can be used to screen the experimental data as well. The new equation developed in this work takes the following form:

$$\Theta x^2 + K_3 x + K_3 K_5 = 0 \qquad (21)$$

Where Θ is a parameter that can be related to the amine concentration, CO_2 loading and partial pressure as follows:

$$\Theta = 1 - \frac{\alpha m_{AMINE}H_{CO_2}}{P_{CO_2}} \qquad (22)$$

114

Table 1: Expressions for constants used in the M-KE model.

Expressions	Rxn no.	Ref
$K_2 = \exp(6.69425 - \dfrac{3.09083E3}{T})$	2-a, MEA	[19]
$K_2 = \exp(4.8255 - \dfrac{1.8848E3}{T})$	2-a, DEA	[19]
$K_3 = \exp\left(-241.818 + \dfrac{298.253E3}{T} - \dfrac{148.528E6}{T^2} + \dfrac{332.648E8}{T^3} - \dfrac{282.394E10}{T^4}\right)$	3-a	[19]
$K_4 = \exp\left(39.5554 - \dfrac{987.9E2}{T} + \dfrac{568.828E5}{T^2} - \dfrac{146.451E8}{T^3} + \dfrac{136.146E10}{T^4}\right)$	4-a	[19]
$K_5 = \exp\left(-294.74 + \dfrac{364.385E3}{T} - \dfrac{184.158E6}{T^2} + \dfrac{415.793E8}{T^3} - \dfrac{354.291E10}{T^4}\right)$	5-a	[19]
$H^o_{CO_2} = \exp\left(22.2819 - \dfrac{138.306E2}{T} + \dfrac{691.346E4}{T^2} - \dfrac{155.895E7}{T^3} + \dfrac{120.037E9}{T^4}\right)$		[19]
$H_{CO_2} = \dfrac{H^o_{CO_2}}{7.50061}$		[19]

Where H_{CO2} and H^o_{CO2} denote the CO₂ Henry's constant in terms of kPa and mmHg, respectively. [19]
Equilibrium constants are concentration based and temperature is in terms of Kelvin.

Table 2: Expressions for constants used in the E-DH and Pitzer models.

Expressions	Rxn/relation no.	Ref.
$K'_1 = 10 \wedge (-14.01 + 0.0184T)$	1-b	[35]
$K'_2 = \exp(2.8898 - \dfrac{3.63509E3}{T})$	2-b, MEA	[36]
$K'_2 = \exp(4.5146 - \dfrac{3.41734E3}{T})$	2-b, DEA	[36]
$K'_3 = \exp(235.482 - \dfrac{12092.1}{T} - 36.7816 \ln T)$	3-b	[29]
$K'_4 = \exp(140.932 - \dfrac{13445.9}{T} - 22.4773 \ln T)$	4-b	[29]
$K'_5 = \exp(220.067 - \dfrac{12431.7}{T} - 35.4819 \ln T)$	5-b	[29]
$K'_{CO_2} = \exp(155.1699 - \dfrac{8477.711}{T} - 21.95743 \ln T + 5.780748E - 3T)$	10	[30]
$A_\phi = -1.306568 + 0.01328238T - 0.3550803E - 4T^2 + 0.3381968E - 7T^3$	11 and 12	[30]

Equilibrium constants are activity based and temperature is in terms of Kelvin.

It is worth mentioning that in the case of $\Theta=0$ and $\Theta>0$ equation (21) does not have physically meaningful roots. In the case $\Theta<0$ equation (21) has a physically meaningful root for the molality of H^+. Therefore, the following criterion for CO_2 loading, α, can be inferred:

$$\Theta=1-\frac{\alpha m_{AMINE}H_{CO_2}}{P_{CO_2}}<0 \tag{23}$$

Or

$$\alpha>\frac{P_{CO_2}}{m_{AMINE}H_{CO_2}} \tag{24}$$

Using this criterion, appropriate experimental data can be selected. If the solubility data meet the criterion, they can be correlated using the M-KE model. *Chakma et al.* [26] presented the solubility of CO_2 in MDEA and BHEP (N, N-Bis (hydroxylethyl) piperazine) aqueous solutions and correlated them with the M-KE model. But some of the data do not satisfy this criterion. Therefore, their proposed relation for pK_1 does not have enough accuracy to predict the CO_2 solubility in the mentioned amine aqueous solutions.

The equilibrium constant for the protonation reaction of the tertiary and sterically hindered amines, K_1, can be calculated using the following equation:

$$K_1=\frac{m_{AMINE}x^3H_{CO_2}}{2K_3K_5P_{CO_2}+\left(K_3P_{CO_2}+K_4H_{CO_2}\right)x-x^3H_{CO_2}}-x \tag{25}$$

One more criterion to select the proper solubility data is based on the above equation:

$$K_1=\frac{m_{AMINE}X^3H_{CO_2}}{2K_3K_5P_{CO_2}+K_4H_{CO_2})x-x^3H_{CO_2}}-x.0 \tag{26}$$

$$P_{CO_2}<\frac{x^3H_{CO_2}+m_{AMINE}x^2H_{CO_2}-K_4H_{CO_2}x}{2K_3K_5+K_3x} \tag{27}$$

Eqs. (24) and (27) are general and can be used to study the solubility of CO_2 in tertiary and sterically-hindered amines. For instance, *Jou et al.* [12] presented the solubility of CO_2 and H_2S in MDEA aqueous solutions at various temperatures and concentrations. A number of experimental data points for CO_2 and H_2S solubility, do not meet Eq. (27).

The proposed criteria, Eqs. (24) and (27), can be used to screen the CO_2 solubility data in the tertiary and sterically hindered amines from the experimental data

reported in the literature. Although pK_1 can be correlated in terms of temperature, amine concentration and CO_2 loading or its partial pressure, in order to calculate CO_2 loading, according to what *Chakma et al.* [26] suggested, the pK_1 must be expressed in terms of the temperature, partial pressure and amine concentration as:

$$pK_1=a+bT+\frac{c}{T}+dLnT+em_{CO_2}+ \tag{28}$$

$$fLnm_{CO_2}+gm_{AMINE}$$

The simplified form for equation (28) can be presented as:

$$pK_1=a+bT+cm_{CO2}+dm_{AMINE} \tag{29}$$

To determine the coefficients of the above equations, the following objective function should be minimized:

$$OF=\sum_{l=1}^{ND}(pK_{1,l}^{exp}-pK_{1,l}^{cal})^2$$

Superscripts exp and cal stand for experimental and calculated values of the equilibrium constant of the amine protonation reaction, respectively. ND is the number of experimental data points.

In this work, the *Davidon-Fletcher-Powell* (DFP) [31] minimization method was used. This method is not sensitive to the initial guess for the interaction parameters and there is no necessity to calculate the second derivative matrix known as the Hessian matrix. Rao [31] presented the iterative procedure of this method.

The relations for pK_1 can be used to obtain CO_2 loading and concentrations for all ions and molecules in the liquid phase using the following equations:

$$F=\frac{K_3P_{CO_2}}{H_{CO_2}x}+\frac{2P_{CO_2}K_3K_5}{H_{CO_2}x^2}+\frac{K_4}{x}-\frac{m_{AMINE}x}{K_1+x} \tag{30}$$

$$\frac{dF}{dx}=\frac{-K_3P_{CO_2}}{H_{CO_2}x^2}-\frac{4P_{CO_2}K_3K_5}{H_{CO_2}x^3}-\frac{K_4}{x^2}-\frac{m_{AMINE}x}{\left(K_1+x\right)^2} \tag{31}$$

$$x=x-\frac{F}{dF/dx} \tag{32}$$

$$\alpha=\frac{K_3K_5P_{CO_2}+P_{CO_2}x^2+P_{CO_2}xK_3}{H_{CO_2}m_{AMINE}x^2} \tag{33}$$

It should be noted that Eq. (30) is only in terms of m_{H^+} and can be solved by the well-known Newton-Raphson method.

116

Since K_1, K_3 and K_5 are small values, the term $P_{CO2}*K_1*K_3*K_5$ is infinitesimal and can be neglected. Therefore, m_H^+ can be determined analytically from the following equation:

$$m_{AMINE}H_{CO_2}x^2 - (K_3H_{CO_2} + K_2P_{CO_2})x - \qquad (34)$$

$$(K_3H_{CO2}K_1 + 2P_{CO_2}K_2K_4 + K_2K_1P_{CO_2}) = 0$$

Having the values for m_H^+, the solubility of CO_2 (α_{CO2}) can be calculated using Eq. (33). The criteria and developed equations can be used to obtain the CO_2 solubility in the tertiary and sterically-hindered amines. To study the solubility of the acid gas in the primary and secondary amine aqueous solutions using the M-KE model, more complicated equations must be used.

The activity coefficients model

Combining Eqs. (1-b) to (5-b), concentrations for all ions and molecules in tertiary and sterically-hindered amines can be expressed only in terms of concentration for H^+ as well as the activity coefficients of the ions and molecules as follows:

$$m_{HCO_3^-} = \frac{K_3'\phi_{CO_2}P_{CO_2}a_w}{H_{CO_2}'x\gamma_{H^+}\gamma_{HCO_3^-}} = \qquad (35)$$

$$\frac{m_{AMINE}\alpha K_3'a_w\gamma_{CO_2}\gamma_H + \gamma_{CO_3^{2-}X}}{D}$$

$$m_{CO_3^{2-}} = \frac{K_3'K_5'\phi_{CO_2}P_{CO_2}a_w}{H_{CO_2}'x^2\gamma_{H^+}^2\gamma_{CO_3^{2-}}} = \frac{m_{AMINE}\alpha K_3'K_5'a_w\gamma_{CO_2}\gamma_{HCO_3^-}}{D} \qquad (36)$$

$$m_{OH^-} = \frac{K_4'a_w}{x\gamma_{H^+}\gamma_{OH^-}} \qquad (37)$$

$$m_{RR'R''NH^+} = \frac{m_{AMINE}x\gamma_{H^+}\gamma_{RR'R''N}}{K_1'\gamma_{RR'R''NH^+} + x\gamma_{H^+}\gamma_{RR'R''N}} \qquad (38)$$

$$m_{RR'R''N} = \frac{m_{AMINE}K_1'\gamma_{RR'R''NH^+}}{K_1'\gamma_{RR'R''NH^+} + x\gamma_{H^+}\gamma_{RR'R''N}} \qquad (39)$$

$$m_{CO_2} = \frac{m_{AMINE}\alpha x^2\gamma_{H^+}^2\gamma_{CO_3^{2-}}\gamma_{HCO_3^-}}{D} \qquad (40)$$

$$P_{CO_2} = \frac{m_{AMINE}\alpha x^2 H_{CO_2}'\gamma_{H^+}^2\gamma_{CO_3^{2-}}\gamma_{HCO_3^-}\gamma_{CO_2}}{D\phi_{CO_2}} \qquad (41)$$

Where D can be expressed according to the following relation:

$$D = (\gamma_{H^+}^2\gamma_{HCO_3^-}\gamma_{co_3^{2-}})x^2 + (K_3'a_w\gamma_{CO_2\gamma_{H^+}}\gamma_{co_3^{2-}})x + \qquad (42)$$

$$K_3'K_5'\gamma_{CO_2}\gamma_{HCO_3^-}a_w$$

To determine x and concentrations for all species present in solution, Eqs. (35)-(38) as well as Eq. (8) were used to develop the following expression:

$$F = x + \frac{m_{AMINE}x\gamma_{H^+}\gamma_{RR'R''N}}{K_1'\gamma_{RR'R''NH^+} + \gamma_{RR'R''N}} - \frac{K_4'a_w}{x\gamma_{H^+}\gamma_{OH^-}} \qquad (43)$$

$$\frac{m_{AMINE}\alpha K_3'a_w\gamma_{CO_2}(2K_5'\gamma_{HCO_3^-} + x\gamma_{H^+}\gamma_{CO_3^{2-}})}{D}$$

To obtain x, Eq. (43) can be solved using the well-known Newton-Raphson method.

To obtain the interaction parameters of the activity coefficients models, the following objective function was minimized using the DFP method:

$$OF = \sum_{l=1}^{ND}\left(\frac{P_{CO_2,l}^{exp} - P_{CO_2,l}^{cal}}{P_{CO_2,l}^{exp}}\right)^2 \qquad (44)$$

where superscripts exp and cal denote the experimental and calculated values for CO_2 partial pressures, respectively.

The following relation was used to obtain the Average Absolute Relative Deviation percent (AARD %) from the corresponding experimental data.

$$AARD\% = \frac{100}{ND}\sum_{l=1}^{ND}\left(\frac{Q_l^{exp} - Q_l^{cal}}{Q_l^{exp}}\right)^2 \qquad (45)$$

In the M-KE model, Q stands for pK_1 while in the E-DH and Pitzer models, Q represents $P_{CO_2}^{exp}$.

To model the solubility of acid gases in the amine aqueous solutions, an arbitrary activity coefficient model along with the new method can be used

The CO_2 loading can also be calculated using the proposed method. To obtain x, Eq. (46) can be solved using the well-known Newton-Raphson method:

$$F = x + \frac{m_{AMINE}x\gamma_{H^+}\gamma_{RR'R''N}}{K_1'\gamma_{RR'R''NH^+} + x\gamma_{H^+}\gamma_{RR'R''N}} - \frac{K_4'a_w}{x\gamma_{H^+}\gamma_{OH^-}} - \qquad (46)$$

$$\frac{K_3'\phi_{CO_2}P_{CO_2}a_w}{H_{CO_2}'x\gamma_{H^+}\gamma_{HCO_3^-}} - \frac{2K_3'K_5'\phi_{CO_2}P_{CO_2}a_w}{H_{CO_2}'x^2\gamma_{H^+}^2\gamma_{CO_3^{2-}}}$$

Table 3: Summary of literature sources of experimental data used to adjust the parameters of M-KE, E-DH and Pitzer models[a].

Solvent	No. of data	Pressure range, kPa	Temp range, ºC	CO_2 loading range	amine concn., M	Sources
MEA	94	0.07- 6100	40-120	0.133-1.19	2.5, 3.0 and 5	[7] and [37]
DEA	193	2- 4400	38-205	0.09-1.167	1.1, 2.4, 3.2 and 4.1	[38] and [39]
MDEA	65	0.88- 1013	40-90	0.01-0.881	3.04, 3.46 and 4.28	[33]
AMP	51	1.59-5645	20-80	0.126-1.216	2, 3 and 3.43	[16] and [18]
AEPD	32	1.8-2849	40-60	0.179-1.289	0.95 and 3.66	[46]
TIPA	69	2.4-2821	40-60	0.201-1.45	0.582 and 2.244	[47]

a) Only the solubility of CO_2 in MDEA aqueous solution were studied using the activity coefficient models.
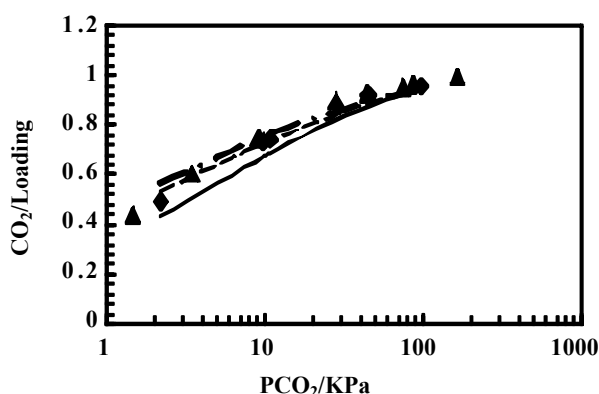

Fig. 1: The solubility of CO_2 in a 2 molar AMP aqueous solutions at 40ºC, (♦) experimental [17], (—) this work Eq. (29), (---) this work Eq. (28), (— - - —) Tontwachwul's work, (▲) experimental [15].

Fig. 2: The solubility of CO_2 in a 6.135 M AMP aqueous solutions at 40ºC, (♦) experimental [41], (—) this work Eq. (29), (---) this work Eq. (28), (— - - —) Tontwachwul's work.

The CO_2 loading can be calculated using the following relation.

$$\alpha_{CO_2} = \frac{1}{m_{AMINE}} \left[\frac{K_3' \phi_{CO_2} P_{CO_2} a_w}{H_{CO_2}' x \gamma_{H^+} \gamma_{HCO_3^-}} + \frac{K_3' K_5' \phi_{CO_2} P_{CO_2} a_w}{H_{CO_2}' x^2 \gamma_{H^+}^2 \gamma_{CO_3^{2-}}} + \frac{\phi_{CO_2} P_{CO_2}}{H_{CO_2}' \gamma_{CO_2}} \right] \qquad (47)$$

RESULTS AND DISCUSSION

In the present study, the solubility data for CO_2 in various types of amine aqueous solutions at various conditions were obtained using the M-KE, E-DH and the Pitzer models. The DFP minimization method was used to determine the parameters introduced in these models. The results showed that the proposed equations along with the DFP minimization method can be used to study the solubility of CO_2 in various types of amines. Table 3
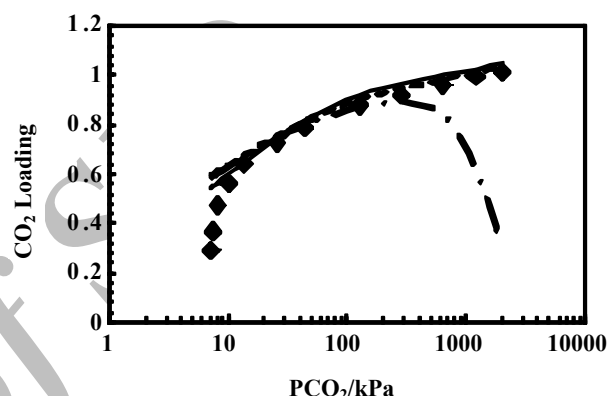
gives in general the types of amine solutions, temperature, pressure and CO_2 loading ranges and number of experimental data points for each specified system used in obtaining the adjustable parameters for the M-KE, E-DH and Pitzer models. It is worth mentioning that the experimental data to be used in tuning the parameters of the models should be screened according to the criteria presented by Eqs. (24) and (27).

Figs. 1 and 2 show the variation of CO_2 loading with CO_2 partial pressure in aqueous AMP solutions with molarity of 2 and 6.135 M at 40ºC, respectively. As observed from Figs: 1 and 2, while at low to moderate CO_2 loading the results obtained from the proposed correlation as well as those obtained by *Tontwachwul et. al.* [18] are in good agreement with the experimental data of CO_2 solubility; at higher CO_2 loadings *Tontwachwul et al.*'s correlation fails to match the experimental data. The deviation of *Tontwachwul's* results from the experimental data begins nearly from

***Table 4: The calculated values of K_1 for MDEA obtained from Chakma's correlation [26] and
Eq. (25) at some experimental point [12].***

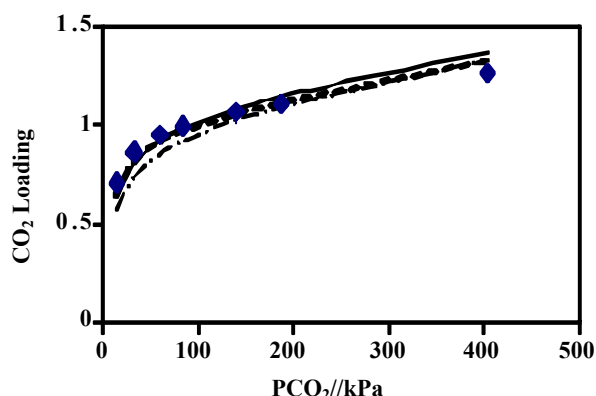| T, °C	m, kmol/m³	α	PCO_2, kPa	K_1 (Chakma's correlation)	K_1 from (Eq. 25)
25	4.28	0.318	5.3	264.80	1.233E-9
40	4.28	0.285	13.3	118.38	3.614E-9
70	2	0.369	40.9	42.22	8.204E-9
100	2	0.502	373.0	11.67	2.143E-8
120	2	0.336	493.0	4.24	5.970E-8

***Fig. 3: The solubility of CO_2 in a 1.9493 M MDEA aqueous
solution at 60°C, (♦) experimental [42], (—) this work Eq. (29),
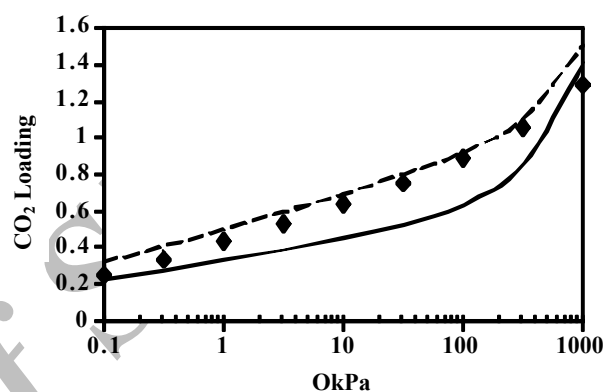(---) this work Eq. (28), (—·—·—) Haji-Sulaiman's relation.***

***Fig. 4: The solubility of CO_2 in a 2 M DEA aqueous solution
at 50°C, (♦) experimental [6], (—) this work Eq. (29), (— — —)
this work Eq. (28).***

α=1 and it strongly depends on the CO_2 loading. Therefore, to predict the solubility of CO_2 in AMP aqueous solutions at low to moderate CO_2 loadings, the proposed and *Tontwachwul's* correlations can be used. Notably, the results of theproposed correlations are more accurate compared to the experimental data at higher CO_2 loading.

Chakma et al. [26] and *Haji-Sulaiman et al.* [32] also studied the solubility of CO_2 in MDEA aqueous solutions using the M-KE model. They also presented correlations for the MDEA equilibrium constant of the protonation reaction. Table 4 shows the MDEA equilibrium constant of the protonation reaction obtained from *Chakma's* correlation [26] and equation (25). As seen from Table 4, *Chakma's* correlation [26] fails to predict the solubility of CO_2 in MDEA aqueous solution accurately.

In this work, new pK_1 correlations of MDEA aqueous solution were presented using the experimental data reported by *Xu et al.* [33]. The Average Absolute Relative Deviation percent (AARD %) of the results obtained from the *Haji-Sulaiman* correlation [32] and the proposed

ones are presented in Table 5. Table 5 shows that the proposed correlations can more accurately represent the experimental data than those of the *Haji-Sulaiman et al.* model. Fig. 3 shows the experimental and calculated CO_2 solubility in MDEA solution with the molarity of 1.9493 at 333.15K. Fig. 3 and Table 5 show that although the *Haji-Sulaiman* [32] and the new correlations can predict the CO_2 loading, the results obtained in this work are more accurate compared with the experimental data. It should be stressed that *Haji-Sulaiman et al.* [34] also presented a correlation for pK_1 of DEA. The correlation is independent of temperature.

Fig. 4 shows the experimental and calculated CO_2 solubility in DEA solutions with the molarity of 2 at 50°C. As seen from this figure, the data obtained from Eq. (28) are more accurate than those obtained from Eq. (29). Therefore, the proposed correlation can be used to predict the solubility of CO_2 in DEA aqueous solution.

The experimental and calculated CO_2 solubility in MEA solutions with the molarity of 2.5 at 25 and 100 °C

119

Table 5: Comparison of the calculated CO_2 solubility in MDEA aqueous solution with the experimental data^a [12].

Correlation	This work, Equation 29	This work, Equation 28	Haji-Sulaiman's correlation
%AARD	17.09	15.44	34.11

^{a} Number of data in this paper is 120.
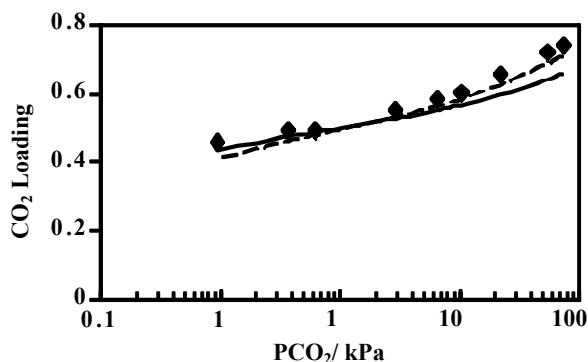
Fig. 5: The solubility of CO_2 in a 2.5 M MEA aqueous solution at 25^oC, (♦) experimental [40], (—) this work Eq. (29), (— — —) this work Eq. (28).
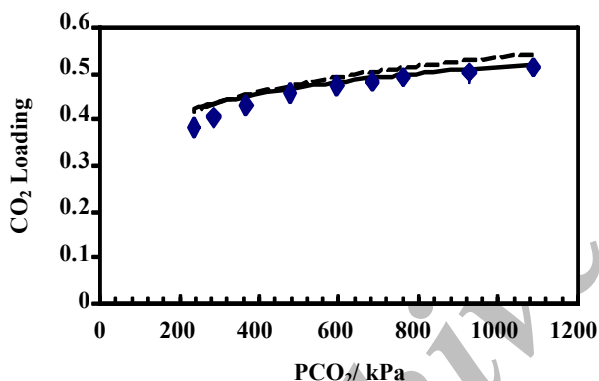
Fig. 6: The solubility of CO_2 in a 2.5 M MEA aqueous solution at 100^oC, (♦) experimental [40], (—) this work Eq. (29), (— — —) this work Eq. (28).
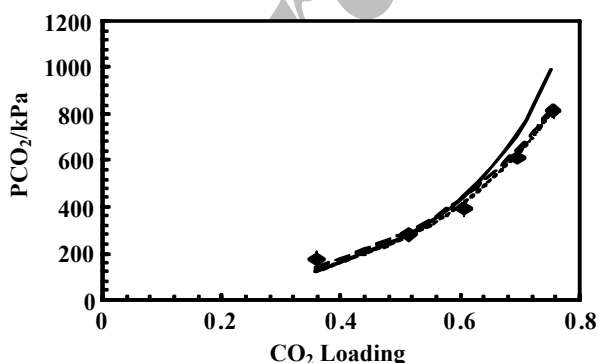
Fig. 7: The solubility of CO_2 in a 3.46 M MDEA aqueous solution at 70^oC, (♦) experimental [33], (——) Pitzer model [33], (— — —) this work E-DH model, (---------) this work Pitzer model.

are presented in Figs. 5 and 6, respectively. As seen from these figures, the results of Eq. (28) are more accurate than those of Eq. (29) to study the solubility of CO_2 in MEA aqueous solutions.

Since the pressure range in Figs. 1, 2, 4 and 5 is wide, the logarithmic scale was used in the x-axis. Otherwise, most of the data would lie near the y-axis.

Tables 6 and 7 present the regressed values for the parameters of Eqs. (28) and (29) for different aqueous amines solutions. These values can be used directly in calculations.

Table 8 presents the binary interaction parameters of the E-DH and Pitzer models in the MDEA-CO_2-H_2O system. In order to obtain the values for the binary interaction parameters, the same experimental data and the same minimization method were used for the models studied in this work.

Fig. 7 compares the experimental CO_2 partial pressures with those calculated using the E-DH and Pitzer models. Fig. 7 also compares the experimental CO_2 partial pressures with those reported by *Xu et al.* As can be inferred from Fig. 7, the models along with the regressed parameters can be used accurately to predict the CO_2 partial pressure.

For simplicity, the concentrations of CO_2 and CO_3^{2-} in the liquid phase were neglected in the Pitzer and E-DH models.

The MDEA-PZ-CO_2-H_2O system was also studied using this method [45].

CONCLUSIONS

The solubility of CO_2 in the primary, secondary, tertiary and sterically hindered amine aqueous solutions at various conditions was studied. In the present work, the Modified Kent-Eisenberg (M-KE), the Extended Debye-Hückel (E-DH) and the Pitzer models were employed to study the solubility of CO_2 in amine aqueous solutions. Two explicit equations are presented to evaluate the concentration of H^+ as well as the equilibrium constants of protonation reactions for the tertiary and sterically hindered amine aqueous solutions. Using the M-KE model, the equilibrium constants of protonation reactions of amines were correlated in terms of temperature, CO_2 partial pressure and amine concentration. Also the E-DH and Pitzer models were used to correlate the solubility of CO_2 in MDEA aqueous solution. The binary interaction

Table 6: Regressed values for the parameters of the M-KE model according to Eq. (28).

Solvent	A	B*100	C	D	E	F*100	G*100	%AARD
MEA	28.2078	-1.1834	-4.4886	-2.5679	-1.3301	2.4310	-2.9575	1.4054
DEA	1464.68	40.875	-35041.3	-256.09	-0.9216	-5.6172	7.8209	2.0645
MDEA	37.546	-0.8176	0.1905	-4.5019	-0.7371	7.4822	-10.512	1.0623
AMP	-246.058	-19.066	-10.111	54.750	-1.1602	-9.9104	6.3486	1.5038
AEPD	639.584	38.305	22.638	-130.65	-3.2094	5.3695	16.7998	1.9216
TIPA	1150.51	70.793	41.660	-237.29	-2.9536	12.979	19.8395	3.9563

Table 7: Regressed values for the parameters of the M-KE model according to Eq. (29).

Solvent	A	B*100	C	D*100	%AARD
MEA	15.5198	-1.8880	-1.1810	-3.0331	1.4931
DEA	11.0907	-1.1020	-1.2172	11.667	2.3428
MDEA	15.438	-2.1162	1.1226	-13.038	1.3120
AMP	14.933	-1.8137	-1.6717	6.9815	1.8404
AEPD	15.708	-2.2844	-2.6963	17.558	2.0967
TIPA	15.948	-2.5246	-1.7994	24.326	4.0018

Table 8: Specific interaction parameters $\beta_{ij}^{(0)}$ for MDEA-CO₂-H₂O in E-DH and Pitzer models.

binary pair [a], kg/mol	E-DH	Pitzer
$\beta(RR'R''N - RR'R''N^+)$	0.0673	0.2624
$\beta(CO_2 - RR'R''N^+)$	-0.0167	0.5046
$\beta(HCO_3^- - RR'R''N^+)$	-1.67E-3	0.1475
$\beta(HCO_3^- - RR'R''N)$	-1.62E-3	-0.1036
$\beta(CO_3^{2-} - RR'R''N^+)$	-0.1001	0.0848
$\beta(CO_3^{2-} - RR'R''N)$	0.0335	0.0897
%AARD	15.973	14.615

a) RR'R''N denotes MDEA.

parameters for the models studied in this work as well as the parameters for the equilibrium constants of protonation reactions were obtained using the *Davidon-Fletcher-Powell* minimization method. The results show that the M-KE, E-DH and the *Pitzer* models can accurately predict the corresponding experimental data.

Although the solubility data for CO_2 in amine aqueous solutions have been reported in the literature to a large extent, accurate data are required to model the CO_2 absorption process. Therefore, two criteria for the tertiary and sterically hindered amines were presented using the M-KE model to screen the experimental data.

The proposed method can also be used to study the amine-H_2S-H_2O systems at various conditions without any additional assumption.

Nomenclature

AARD%   Average absolute relative deviation percent
a_w Activity of water, mol/kg
A_ϕ Constant in the E-DH and Pitzer equations
H   Henry's constant, kmol/(m³.kPa) in the M-KE model
H́   Henry's constant, kmol/(m³.kPa)
     in the activity coefficient model
I   Ionic strength, mol/kg

121

K	Equilibrium constant in the M-KE model
Ḱ	Equilibrium constant in the activity coefficient models
M_w	Molecular weight of water, 0.018 kg/mol
m_i	Molality, mol/kg of solvent
m_{AMINE}	Total concentration of the tertiary and sterically hindered amines, (kmol/m^3)
m_{A1}	Total concentration of the primary and secondary amines, (kmol/m^3)
nc	Number of com
nd	Number of data
OF	The objective function to determine the parameters of models
P_{CO2}	Partial pressure of CO_2, (kPa)
Q	Thermodynamic variable such as pK_1 in the M-KE model and P_{CO2} in the activity coefficient model to calculate AARD%
T	Temperature, (K)
x	The concentration of H^+
Z_i	Ionic charges on species i

Greek symbols

α	CO_2 loading, mol of CO_2 / mol of amine
β	The interaction parameters in the E-DH model
$\beta^{(0)}$, $\beta^{(1)}$	The interaction parameters in the Pitzer model
γ	Molar activity coefficients
Θ	The coefficient of x^2 in the equation 21
φ	Vapor phase fugacity coefficient of CO_2

Superscript

´	The properties in the activity coefficient model such as Ḣ, Ḱ and etc.
exp	Experimental
cal	Calculated

Subscript

i, j	Species or component
l	the number of experimental datum
w	water

Amine abbreviations

MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
DEA	Diethanolamine
AMP	2-amino-2-methyl-1-propanol
TIPA	Triisopropanolamine
AEPD	2-amino-2-ethyl-1, 3-propanediol

RR′R″N	The tertiary or sterically hindered amines
RR′NH	The secondary amine such as DEA
RNH_2	The primary amine such as MEA
RR′NCOO$^-$	Carbamate ion in the primary or Secondary amines systems

Models abbreviations

M-KE	The modified Kent-Eisenberg model
E-DH	The extended Debye-Hückel model

REFERENCES

[1] Guevara F.M., Libreros\, M.E.R., Martínez A.R., Trejo A., Solubility of CO_2 in Aqueous Mixtures of Diethanolamine with MDEA and 2-Amino-2-Methyl-1-Propanol, *Fluid Phase Equlibria,* **150-151**, 721 (1998).

[2] Sartori G., Savage D.W., Sterically Hindered Amines for CO_2 Removal from Gases*, I&EC Fundam.,* **22**, 239 (1983).

[3] Lee J.I., Otto F.D., Mather A.E., Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at High Pressures, *J. Chem. Eng. Data,* **17** (4), p. 465 (1972).

[4] Woertz B.B., Experiments with Solvent-Amine-Water for Removing CO_2 from Gas, *Can. J. Chem. Eng.,* **50**, 425 (1972).

[5] Lee J.I., Otto F.D., Mother A.E., Partial pressures of Hydrogen Sulfide over Aqueous Diethanolamine Solutions, *J. Chem. Eng. Data,* **18** (4), 420 (1973).

[6] Lee J.I., Otto F.D., Mather A.E., The Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulphide in Aqueous Diethanolamine Solutions, *Can. J. Chem.Eng.,* **52**, 125 (1974).

[7] Lee J.I., Otto F.D., Mather A.E., The Solubility of H_2S and CO_2 in Aqueous Monoethanolamine Solutions, *Can. J. Chem. Eng.,* **52**, 803 (1974).

[8] Lee J.I., Otto F.D., Mather A.E., "The Measurement and Prediction of the Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 2.5N Monoethanolamine Solution, *Can. J. Chem. Eng.,* **54**, 214 (1976).

[9] Nasir P., Mather A.E., The Measurement and Prediction of the Solubility of Acid Gases in Monoethanolamine Solution at Low Partial Pressures, *Can. J. Chem. Eng.,* **55**, 715 (1977).

[10] Isaacs E.E., Otto F.D., Mather A.E., Solubility of Mixtures of H₂S and CO₂ in a Monoethanolamine Solution at Low Partial Pressures, *J. Chem. Eng. Data,* **25**, 118 (1980).

[11] LAL D., Otto F.D., Mather A.E., The Solubility of H₂S and CO₂ in a Diethanolamine Solution at Low Partial Pressures, *Can. J. Chem. Eng.,* **63**, 681 (1985).

[12] Jou F.Y., Mather A.E., Otto F.D., Solubility of H₂S and CO₂ in Aqueous Methyldiethanolamine Solutions, *Ind. Eng. Chem. Process Des, Dev.,* **21**, 539 (1982).

[13] Jou F.Y., Carroll J.J., Mather A.E., Otto F.D., Solubility of Mixtures of Sulfide and Carbon Dioxide in Aqueous *N*-Methyldiethanolamine Solutions, *J. Chem. Eng. Data,* **38**, 75 (1993).

[14] Jou F.Y., Carroll J.J., Mather A.E., Otto F.D., The Solubility of Carbon Dioxide and Hydrogen Sulfide in a 35% Aqueous Solution of Methyldiethanolamine, *Can. J. Chem. Eng.*, **71**, 264 (1993).

[15] Jane I.S., Li M.H., Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in Water + Diethanolamine + 2-Amino-2-Methyl-1-Propanol, *J. Chem. Eng. Data,* **42** (1), 98 (1997).

[16] Teng T.T., Mather A.E., Solubility of H₂S , CO₂ and Their Mixtures in an AMP Solution, *Can. J. Chem. Eng.*, **67**, 846 (1989).

[17] Roberts B.E., Mather A.E., Solubility of *CO₂* and H₂S in a Hindered Amine Solution, *Chem. Eng. Comm.,* **64**, 105 (1988).

[18] Tontlwachwuthlkul P., Meisen A., Lim C.J., Solubility of CO₂ in 2-Amino-2-methyl-1-propanol Solutions, *J. Chem. Eng. Data,* **36**, 130 (1991).

[19] Kent R.L., Eisenberg B., Better data for amine treating, *Hydrocarbon process.,* **55** (2), 87 (1976).

[20] Deshmukh R.D., Mather A.E., A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions, *Chem. Eng. Sci.,* **36**, 355 (1981).

[21] Pitzer K.S., Thermodynamics of Electrolytes I. Theoretical Basis and General Equations, *J. phys. Chem,* **77** (2), 268 (1973).

[22] Pitzer, K.S. and Kim, J.J.; Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients of Mixed Electrolytes, *J. Am. Chem. Soc*, **96** (18), 5701 (1974).

[23] Hyden J.G., O´Connell J.P., A Generalized Method for Predicting Second Virial Coefficients, *Ind. Eng. Chem. Process Des. Dev.,* **14** (3), 209 (1975).

[24] Peng D.Y., Robinson D.B., A new Two Constant Equation of State, *Ind .Eng .Chem., Fundam.,* **15** (1), 59 (1976).

[25] Soave G., Equilibrium Constants from a Modified Redlich-Kwong Equation of State, *Chem. Eng. Sci.,* **27**, 1197 (1972).

[26] Chakma A., Meisen A., Solubility of CO₂ in Aqueous Methyldiethanolamine and N,N-Bis(hydroxyethyl) piperazine Solutions, *Ind. Eng. Chem. Res.,* **26**, 2461 (1987).

[27] Sartori G., Savage D.W., Sterically Hindered Amines for CO₂ Removal from Gases, *I & EC Fundam.,* **22**, 239 (1983).

[28] Chakraborty A. K.; Astarita, G. and Bischoff, K.B.; CO₂ Absorption in Aqueous Solutions of Hindred Amines, *Chem. Eng. Sci.,* **41** (4), 997 (1986).

[29] Edwards T.J., Maurer G.G., Newman G., Prausnitz J.M., Vapor-Liquid Equlibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes, *AIChE,* **24** (6), 966 (1978).

[30] Chen C.C., Britt H.I., Boston J.F., Evans L.B., Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte System with Molecular Solute, *AIChE,* **25** (5), 820 (1979).

[31] RAO S.S., "Optimization Theory and Applications", Second ed. Wiley Eastern Limited, pp. 509-516 (1984).

[32] Haji-Sulaiman M.Z., Aroua M.K., Analysis of Equilibrium Data of CO₂ in Aqueous Solutions of Diethanolamine (DEA) ,Methyldiethanolamine (MDEA) and Their Mixtures Using the Modified Kent Eisenberg Mode, *Trans. Inst. Chem. Eng.,* **76**, 961 (1998).

[33] Xu G.W., Zhang C.F., Qin S.J., Gao W.H., Liu H.B., Gas-Liquid Equilibrium in a CO₂-MDEA-H₂O System and the Effect of Piperazine on it, *Ind. Eng. Chem. Res.,* **37** (4), 1473 (1998).

[34] Haji-Sulaiman M.Z., K.Aroua M., Pervez M.L., Equlibrium Concentration Profiles of Species in CO2-Alkanolamine-Water Systems, *Gas. Sep. Purif.,* **10** (1), 13 (1996).

123

[35] Barth D., Tondre C., Delpuech J.J., Kinetics and Mechanisms of the Reactions of Carbon Dioxide with Alkanolamines: A Discussion Concerning the Cases of MDEA and DEA, *Chem. Eng. Sci.,* **39** (12), 1753 (1984).

[36] Austgen D.M., Rochelle G.T., Chen C.C., Model of Vapor-Liquid Equlibria for Aqueous Acid Gas-Alkanolamine Systems. 2.Representation of H_2S and CO_2 Solubility in Aqueous MDEA and CO_2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA, *Ind. Eng. Chem. Res.,* **30**, 543 (1991).

[37] Jones J.H., Froning H.R., Claytor E.E.Jr., Solubility of Acidic Gases in Aqueous Mono-ethanolamine, *J. Chem. Eng. Data,* **4** (1), 85 (1959).

[38] Lawson J.D., Garst A.W., "Gas Sweetening Data: Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Monoethanolamine and Diethanolamine Solutions*", J.Chem. Eng.Data*, **21** (1), 20 (1976).

[39] Kennard M. L., Meisen A., Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at Elevated Temperatures and Pressures, *J. Chem. Eng. Data,* **29** (3), 309 (1984).

[40] Muhlbauer H.G., Monaghan P.R., New Equilibrium Data On Sweetening Natural Gas With Ethanol amine Solutions, *The Oil And Gas Journal,* **55** (17) ,139 (1957).

[41] Silkenbaumer D., Rumpf B., Lichtenthaler R.N., Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-Methyl-1-Propanol and *N*-Methyldiethanolamine and Their Mixtures in the Temperature Range 313 to 413 K and Pressures up to 2.7MPa*, Ind. Eng. Chem. Res.,* **37** (8), 3133 (1998).

[42] Kuranov G., Rumpf B., Smirnova N.A., Maurer G., Solubility of Single Gases Carbon Dioxide and Hydrogen Sulfide in Aqueous Solutions of *N*-Methyldiethanolamine in the Temperature Range 313-413 K at Pressures up to 5MPa*, Ind. Eng. Chem. Res.,* **35** (6), 1959 (1996).

[43] Li Y.G., Mather A.E., Correlation and Prediction of the Solubility of CO_2 in a Mixed Alkanolamine Solution, *Ind. Eng. Chem. Res.,* **33**, 2006 (1994).

[44] Kamps A.P.S., Balaban A., Jödecke M., Kuranov G., Smirnova N.A., Maurer G., Solubility of Single Gases Carbon Dioxide and Hydrogen Sulfide in Aqueous Solutions of *N*-Methyldiethanolamine at Temperatures from 313 to 393K and Pressures up to 7.6 Mpa: New Experimental Data and Model Extension, *Ind. Eng. Chem. Res.,* **40** (2), 696 (2001).

[45] Seyed Matin N., Goharrokhi M., Vahidi M., Hosseini Jenab M., Najibi S.H., Abedinzadegan Abdi M., Solubility of CO_2 in Aqueous Solutions of N-Methyldiethanolamine + Piperazine Using Extended Debye-Hückel Model, *Japanian Journal of Chemical Eng.,* **40** (2), 2007.

[46] Park J.Y., Yoon S.J., Lee H., Yoon J.H., Shim J.G., Lee J.K., Min B.Y., Eum H.-M., Kang M.C., Solubility of Carbon Dioxide in Aqueous Solutions of 2-Amino-2-Ethyl-1,3-Propanediol, *Fluid Phase Equlibria,* **202**, 359 (2002).

[47] Chauhan R.K., Yoon S.J., Lee H., Yoon J.-H., Shim J.-G., Song G.-C., Eum H.-M., Solubility of Carbon Dioxide in Aqueous Solutions of Triisopropanolamine, *Fluid Phase Equlibria,* **208**, 239 (2003).