A Thermodynamic Model for Determination of Carbon Dioxide Solubility and Ionic Speciation in Aqueous Alkanolamine Solutions

Humbul Suleman, Abdulhalim Shah Maulud* and Zakaria Man
Department of Chemical Engineering, Universiti Teknologi Petronas, 32610
Bandar Seri Iskandar, Perak, Malaysia.
halims@utp.edu.my*

Summary: A thermodynamic model for determination of carbon dioxide solubility and liquid phase ionic speciation in aqueous alkanolamine solutions has been presented. The explicit model equation is simple in computation and can be solved using a hand-held calculator, yet its structure is derived from thermodynamic theory. The model predicts liquid phase ionic equilibria (bicarbonate, carbonate, hydrogen and alkanolamine based species) in carbon dioxide loaded aqueous monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) solutions. The model shows good correlation with experimental data points and is valid for carbon dioxide loadings of 0.001 to 0.9 for MDEA and AMP, and 0.002 to 0.48 for MEA and DEA, over a wide range of amine concentration, pressure and temperature. The equilibrium model developed in this work is based on and represents 159 data points for CO_2 solubility in MEA solutions with 7.9% AARD, 114 selected data points for CO_2 absorption in aqueous DEA solutions with 7.1% AARD, 107 reported values for CO_2 solubility in MDEA solutions with 9.9% AARD and 136 data values for CO_2 absorption in aqueous AMP solutions with 8.4% AARD.

Keywords: Alkanolamine; Equilibrium modeling; Carbon capture; Absorption; Ionic equilibrium.

Introduction

Separation of carbon dioxide by aqueous alkanolamine solutions has proven its technological provenance. The technique is extensively utilized in industrial carbon capture processes due to their ease in operation and capital savings. It operates using a dual absorptive and desorptive step, where the carbon dioxide is removed by absorption in an alkanolamine and then desorbed in two separate columns, respectively. Both columns operate at different process conditions. The absorption stage in a carbon dioxide removal system is operated at low temperature and high pressure conditions. Contrarily, the desorption stage operates at high temperature and low pressure to discharge the absorbed gas from the solvent. The overall operation becomes a complex optimization algorithm where high capacity of absorption is favorable but it results in temperature increase at absorption stage (reducing absorption). Hence, the loadings (mole of carbon dioxide absorbed per mole of alkanolamine) of alkanolamine solutions are kept low (0.2 – 0.4) to avoid excessive generation of heat and heavy pumping costs [1]. The use of alkanolamines has increased rapidly after the ratification of environmental protocols and associated global warming [2]. Monoethanolamine was once the solvent of choice for the separation of carbon dioxide in industrial applications. However, its corrosive nature allowed diethanolamine (DEA) and N-methyldiethanolamine (MDEA) to gain widespread use [3]. Recently, 2-amino-2-methyl-1-propanol

(AMP) has shown promising results as a choice of solvent for carbon dioxide capture [4].

One of the biggest challenges in design and development of carbon dioxide absorption/desorption systems is the definition of critical process parameters at early stage, like, operating conditions, energy requirements and phase speciation. These parameters control equipment sizing, design and process integration. Thus, precise thermodynamic modeling of the vapor liquid equilibrium (VLE) is mandatory. A thermodynamic model should satisfactorily predict the solubility of carbon dioxide in alkanolamines and reactive ionization of carbon dioxide in liquid phase. This knowledge helps in the better understanding of kinetic and transport properties, leading to the optimal design of absorption/desorption systems.

Kent and Eisenberg [5] is one of the first widely used model that predicted ionic equilibria and carbon dioxide loadings in aqueous MEA and DEA solutions. They adopted published equilibrium constants from literature for all reactions, except protonation and carbamation of alkanolamines. These two values were deemed apparent equilibrium constants and were fitted to the experimental data in a set of iterative equations. The gas concentration in liquid phase was determined by the Henry's law. Jou *et al.* [6] extended the model to tertiary

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*To whom all correspondence should be addressed.

alkanolamines. The Kent and Eisenberg model was modified in a polynomial form by various researchers [7-9]_ENREF_7_ENREF_13_ENREF_14.

Deshmukh and Mather [10] created a rigorous model, accounting for activity coefficients and fugacity correlations for all ionic species in MEA solutions. Austgen *et al.* [11] and Faramarzi *et al.* [12] used electrolyte NRTL and extended UNIQUAC to correlate carbon dioxide solubility in alkanolamine solutions, respectively. These models used separate equations to correlate vapor (equation of state) and liquid (activity coefficient) phases.

Vallee *et al.*[13] and Chunxi and Furst [14] used the electrolyte equation of state to predict carbon dioxide VLE in aqueous DEA and MDEA solutions, respectively. Vrachnos *et al.* [15] developed electrolyte LCVM model for the discussed system. Recently, Zoghi *et al.*[16] used cubic plus association equation of state to correlate VLE of carbon dioxide-alkanolamine-water system. These models employed single equation of state in conjunction with the mixing rules to relate vapor and liquid fugacities. A detailed review of the aforementioned techniques can be seen in [17].

Common features among the aforementioned models are their complex nature and regression of adjustable parameters to the experimental data. Hence, these models are localized in performance and extrapolation beyond range is conditional. All models comprise of nonlinear equations that have to be solved simultaneously. This is not only computationally intricate but also time intensive. Moreover, it is hard to justify the use of such complex algorithms, when the quality of experimental data is uncertain and large variances are frequent in published literature [18]. Considering these factors, Posey *et al.*[19] and Gabrielsen *et al.* [20] presented simple explicit models for predicting carbon dioxide solubility in alkanolamines. These models consisted of a single chemical equilibrium reaction equation with good correlation. However, they neglected other chemical reactions in the system and assumed that only a single ion (bicarbonate) represented the formation of other ionic species, like carbonate, hydroxide, hydrogen and alkanolamine based ions. This assumption simplifies the model. However, it contradicts with the established theory and their models could not correlate the ionic speciation. Moreover, both researchers neglected the physical absorption of carbon dioxide in the system.

The objective of this study is to develop a simple explicit model for determination of carbon
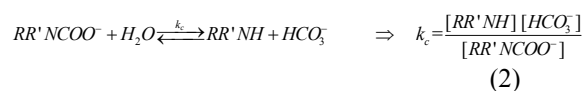
dioxide solubility and liquid phase ionic equilibria in aqueous alkanolamine solutions simultaneously. The model uses a single combined equilibrium reaction equation and accounts for published equilibrium constants for each reaction in the system. The approach simplifies the VLE calculations, as a single explicit equation is solved for determination of hydrogen ion. The value of hydrogen ion concentration is then used in consequent equilibrium constant equations to calculate ionic equilibria and carbon dioxide solubility. This model can be regarded as a combination of Gabrielsen model [20] and Kent Eisenberg model [5] for simple correlation of carbon dioxide solubility and liquid phase ionic speciation.

In this work, carbon dioxide solubilities and ionic speciation has been correlated in aqueous solutions of MEA, DEA, MDEA and AMP. Since primary (MEA) and secondary (DEA) form carbamate upon reaction with carbon dioxide, their model framework has been developed separately from tertiary (MDEA) and sterically hindered (AMP) type alkanolamines [8, 21].

Thermodynamic Framework

Chemical Equilibrium of Carbon Dioxide-MEA/DEA- Water

The reaction mechanisms of carbon dioxide-MEA/DEA-water system can be generally written as given below in Eqs. (1-5).

$$RR'NH_2^+ \overset{k_1}{\rightleftharpoons} RR'NH + H^+ \quad \Rightarrow \quad k_1 = \frac{[RR'NH][H^+]}{[RR'NH_2^+]} \tag{1}$$

$$RR'NCOO^- + H_2O \overset{k_c}{\rightleftharpoons} RR'NH + HCO_3^- \quad \Rightarrow \quad k_c = \frac{[RR'NH][HCO_3^-]}{[RR'NCOO^-]} \tag{2}$$

$$CO_2 + H_2O \overset{k_2}{\rightleftharpoons} HCO_3^- + H^+ \quad \Rightarrow \quad k_2 = \frac{[HCO_3^-][H^+]}{[CO_2]} \tag{3}$$

$$HCO_3^- \overset{k_3}{\rightleftharpoons} CO_3^{-2} + H^+ \quad \Rightarrow \quad k_3 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]} \tag{4}$$

$$H_2O \overset{k_4}{\rightleftharpoons} H^+ + OH^- \quad \Rightarrow \quad k_4 = [OH^-][H^+] \tag{5}$$

where $RR'NH$, $_{RR'NH_2^+}$ and $RR'NCOO^-$ represents the free, protonated and carbamate forms of primary and secondary alkanolamines. Since the degree of

ionization for water is very small as compared to its presence in bulk quantity, reaction 5 is neglected. So, combining Eqs.(1-4) for MEA and DEA reveals the chemical equilibrium reaction given in Eq. (6).

$$RR'NH_2^+ + RR'NCOO^- + CO_2 + 2H_2O \overset{K}{\rightleftharpoons} 2RR'NH + 3H^+ + HCO_3^- + CO_3^{-2}$$
(6)
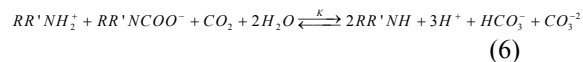
And K is the combined equilibrium constant for the reactions given in Equations 1 to 4 is defined in Eq. (7).

$$K = k_1 . k_c . k_2 . k_3 . f$$
(7)

where f is the adjustment parameter. By introducing the values of equilibrium constants of individual reactions and simplifying yields Eq. (8).

$$k_1.f = \frac{[RR'NH][H^+]}{[RR'NH_2^+]}$$
(8)

The balances for total carbon dioxide concentration, $[CO_2]_{Total}$ and alkanolamine concentration $[RR'NH]_{Total}$ can be expressed in Eq.(9) and Eq. (10), respectively.

$$[CO_2]_{Total} = \alpha[RR'NH]_{Total} = [CO_2]_{physical} + [CO_2]_{ionic}$$
(9)

$$[RR'NH]_{Total} = [RR'NH_2^+] + [RR'NCOO^-] + [RR'NH]$$
(10)

where α is the carbon dioxide loading, $[CO_2]_{physical}$ and $[CO_2]_{ionic}$ is the molar concentration of carbon dioxide in the physical and ionic forms (bicarbonate, carbonate, carbamate) in an aqueous solution, respectively. $[CO_2]_{physical}$ is determined by the Henry's law, given in Eq. (11), whereas, the ionized form of carbon dioxide in liquid phase, $[CO_2]_{ionic}$ is calculated by Eq. (12).

$$[CO_2]_{physical} = \frac{P_{CO2}}{k_H}$$
(11)

$$[CO_2]_{ionic} = [HCO_3^-] + [CO_3^{-2}] + [RR'NCOO^-]$$
(12)

where P_{CO2} is the vapor pressure of carbon dioxide and k_H is the Henry's constant.

The alkanolamine concentrations can be written as a function of physically absorbed CO_2 and carbon dioxide loadings in liquid phase [20].

$$[RR'NH_2^+] = [RR'NCOO^-] = \alpha[RR'NH]_{Total} - [CO_2]_{physical}$$
(13)

$$[RR'NH] = [RR'NH]_{Total} - 2\alpha[RR'NH]_{Total} + 2[CO_2]_{physical}$$
(14)

Hence, Eq. (8) can be written as follows;

$$[H^+] = \frac{k_1.f(\alpha[RR'NH]_{Total} - [CO_2]_{physical})}{([RR'NH]_{Total} - 2\alpha[RR'NH]_{Total} + 2[CO_2]_{physical})}$$
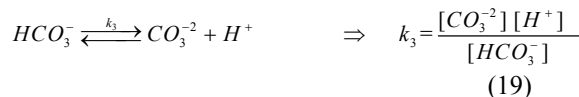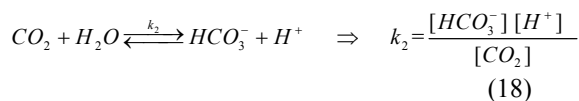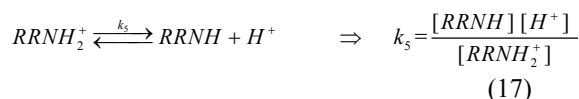(15)

The value of hydrogen ion $[H^+]$ is used to determine the concentrations of bicarbonate, and carbonate from equilibrium constant equations, in Eqs. (3-4). The carbamate concentration is determined by Eq. (16).

$$[RR'NCOO^-] = \frac{[H^+]([RR'NH]_{Total} - 2\alpha[RR'NH]_{Total} + 2[CO_2]_{physical})}{k_1.f}$$
(16)

The values of $[CO_2]_{physical}$ and $[CO_2]_{ionic}$ are summated in Eq. (9) to find $[CO_2]_{Total}$.

Chemical Equilibrium of Carbon Dioxide-MDEA/AMP-Water

The reaction mechanisms of carbon dioxide-MDEA/AMP-water system can be generally written in Eqs. (17-20).

$$RRNH_2^+ \overset{k_5}{\rightleftharpoons} RRNH + H^+ \quad \Rightarrow \quad k_5 = \frac{[RRNH][H^+]}{[RRNH_2^+]}$$
(17)

$$CO_2 + H_2O \overset{k_2}{\rightleftharpoons} HCO_3^- + H^+ \quad \Rightarrow \quad k_2 = \frac{[HCO_3^-][H^+]}{[CO_2]}$$
(18)

$$HCO_3^- \overset{k_3}{\rightleftharpoons} CO_3^{-2} + H^+ \quad \Rightarrow \quad k_3 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]}$$
(19)

$$H_2O \overset{k_4}{\rightleftharpoons} H^+ + OH^- \quad \Rightarrow \quad k_4 = [OH^-][H^+]$$
(20)

Since the ionization of water is quite low in comparison to its high content in the mixture, Eq. (20) is neglected. Remaining equations are combined to a single chemical equilibrium reaction shown in Eq. (21).

$$RRNH_2^+ + CO_2 + H_2O \overset{K}{\rightleftharpoons} RRNH + 3H^+ + CO_3^{-2} \quad (21)$$
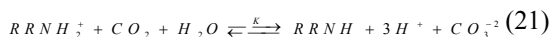
And K is the combined equilibrium constant for the reaction and defined in Eq. (22).

$$K = k_5 . k_2 . k_3 . f \qquad (22)$$

where f is the adjustment parameter. By introducing the values of equilibrium constants of individual reactions and simplifying gives Eq. (23).

$$k_5 . f = \frac{[RRNH][H^+]}{[RRNH_2^+]} \qquad (23)$$

The balances for total carbon dioxide concentration, $[CO_2]_{Total}$ and alkanolamine concentration $[RRNH]_{Total}$ can be expressed in Eqs. (24-25).

$$[CO_2]_{Total} = \alpha [RRNH]_{Total} = [CO_2]_{physical} + [CO_2]_{ionic} \qquad (24)$$

$$[RRNH]_{Total} = [RRNH_2^+] + [RRNH] \qquad (25)$$

$[CO_2]_{physical}$ and $[CO_2]_{ionic}$ is determined by Equation 11 and Equation 26, respectively.

$$[CO_2]_{ionic} = [HCO_3^-] + [CO_3^{-2}] \qquad (26)$$

The alkanolamine concentrations can be given as a function of physically absorbed CO_2 and carbon dioxide loading in liquid phase [19].

$$[RRNH_2^+] = \alpha [RRNH]_{Total} - [CO_2]_{physical} \qquad (27)$$

$$[RRNH] = [RRNH]_{Total} - \alpha [RRNH]_{Total} + [CO_2]_{physical} \qquad (28)$$

Hence, Eq. (23) can be re-written as follows.

$$[H^+] = \frac{k_5 . f \, (\alpha [RRNH]_{Total} - [CO_2]_{physical})}{([RRNH]_{Total} - \alpha [RRNH]_{Total} + 2[CO_2]_{physical})} \qquad (29)$$

The value of hydrogen ion $[H^+]$ is used to determine the concentrations of bicarbonate and carbonate from equilibrium constant equations, in Eqs. (19-20). The values of $[CO_2]_{physical}$ and $[CO_2]_{ionic}$ are added in Eq. (24) to find $[CO_2]_{Total}$.

Model Parameters

Equilibrium constants, including the Henry's constant were determined by Eq. (30)[22].

$$k_i = \exp(a_i / T + b_i \ln T + c_i T + d_i) \quad (30)$$

The adjustment factor f for all alkanolamines (MEA, DEA, MDEA and AMP) is given by Eq. (31).

$$\ln f = A + B\alpha + C\sqrt{\alpha} + D[CO_2]_{physical} \qquad (31)$$

All the adjustable parameters involve the carbon dioxide loading and physical absorption of carbon dioxide to approximate an ionic strength dependence to account for non-idealities in the system, as suggested by Posey *et al.* [19] and Gabrielsen *et al* [20]. The parameter, D is only applicable for systems containing MDEA and AMP. Experimental data from various sources was collected and studied [17]. However, sources reporting their majority of data values below loadings of 0.9 for MDEA and AMP, and 0.48 for MEA and DEA solutions were only selected. The selected sources, presented in Table-2 were included in parameter regression for carbon dioxide loadings between 0.001 to 0.9 for MDEA and AMP, and 0.002 to 0.48 for MEA and DEA solutions. The adjustment factor, f was calculated from the objective function, OF by using a Levenberg-Marquardt routine in Eq. (32).

$$OF = \frac{1}{N} \sum_{N=1}^{N} \left([CO_2]_{calc} - [CO_2]_{exp}\right)^2 \qquad (32)$$

where $[CO_2]_{calc}$ and $[CO_2]_{exp}$ are the calculated and the experimental total carbon dioxide solubility, respectively. The values of regressed parameters A to D for each CO_2-alkanolamine-H_2O systems and their average absolute relative percentage deviation (AARD%) are given in Table-3.

Table-1: Values of constants for Eq. (30).

Parameter	a	b	c	d	Source
k_{1MEA}	-3090.83	0	0	6.69425	Aboudheir*et al.* [24]
k_{CMEA}	-5851.11	0	0	-3.3636	Aboudheir*et al.* [24]
k_{1DEA}	-3071.15	6.7769	0	-48.7594	Haji Sulaiman *et al.* [8]
k_{CDEA}	-17067.2	-66.8007	0	439.709	Haji Sulaiman *et al.* [8]
k_2	-12091.2	-36.7816	0	235.482	Edwards *et al.* [22]
k_3	-13445.9	-22.4773	0	140.932	Haji Sulaiman *et al.* [22]
k_{5MDEA}	-8483.95	-13.8328	0	87.3972	Edwards *et al.* [8]
k_{5AMP}	-4317.27	2.11349	0	-18.0751	Haji Sulaiman *et al.* [25]
k_H	-6789.04	-11.4519	-0.0105	94.4914	Haji Sulaiman *et al.* [22]

Table-2: Sources of experimental data used for parameter regression.

System	Amine Concentration (wt%)	Temperature (K)	No. of Data Points	Source
CO₂-MEA-H₂O	15, 30, 45, 60	313.2 – 373.2	122	Aronu *et al.* [26]
	30.5	373.2	37	Nasir and Mather [27]
CO₂-DEA-H₂O	41.8	298.2 – 348.2	28	Sidi-Boumedine *et al.* [28]
	5.25, 20,6, 35.4, 49.8, 77.6	298.2 – 373.2	86	Lee *et al.* [29]
CO₂-MDEA-H₂O	35.1, 40.2, 48.9	313.2 – 373.2	65	Xu *et al.* [30]
	23.4, 46.1	303.2 – 323.2	42	Haji Sulaiman *et al.* [8]
CO₂-AMP-H₂O	17.6, 25.8	293.2 – 353.2	38	Tontiwachwuthikul *et al.* [31]
	22.5, 30.4, 42.9	298.2 – 328.2	98	Dash *et al.* [4]

Table-3: Values of regressed parameters for different carbon dioxide-alkanolamine-water systems.

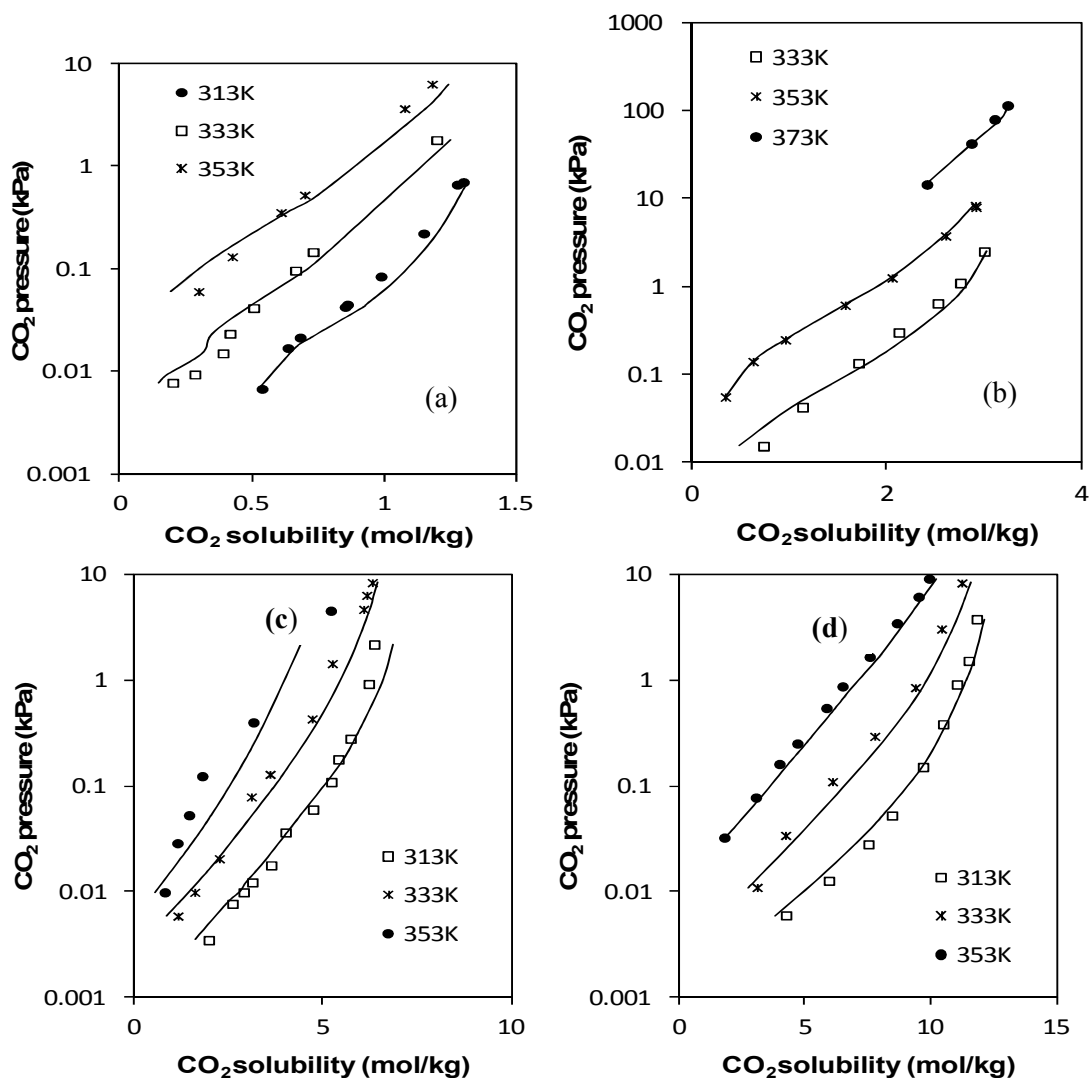| System	A	B	C	D	AARD%
CO₂-MEA-H₂O	0.0073	0.0042	0.0035	0	7.9
CO₂-DEA-H₂O	0.0218	-0.0215	-0.0032	0	7.1
CO₂-MDEA-H₂O	1.5307	1.2019	-4.3167	3.9505	9.9
CO₂-AMP-H₂O	1.5608	1.4995	-2.3157	1.9854	8.4

Fig. 1:   Comparison of model correlation (solid lines) with experimental carbon dioxide solubility in aqueous (a) 15 wt%, (b) 30 wt%, (c) 45 wt% and (d) 60% MEA solutions [26].
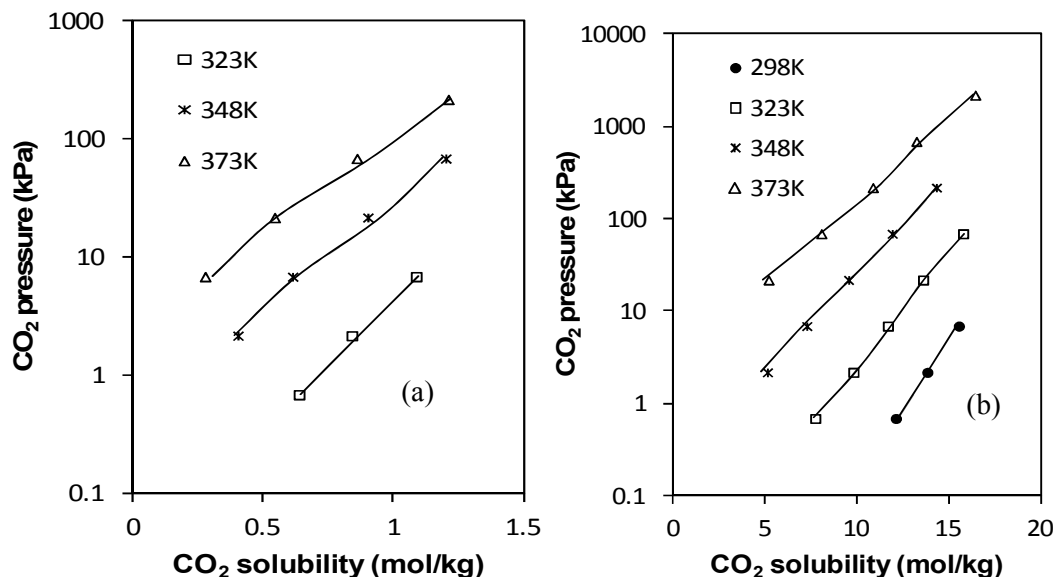
Fig. 2:   Comparison of model correlation (solid lines) with experimental carbon dioxide solubility in aqueous (a) 20.6% and (b) 77.6% DEA solutions [29].
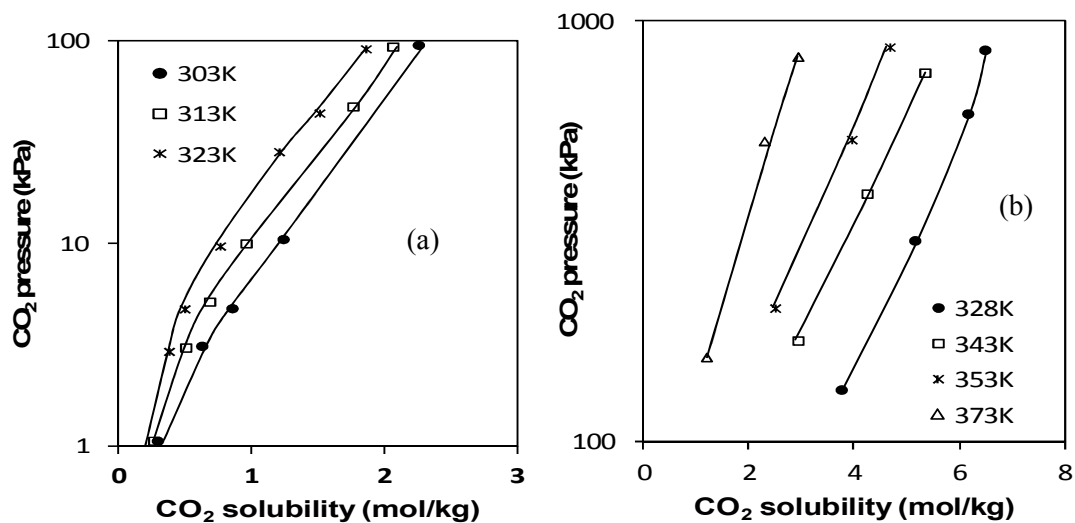

Fig. 3:   Comparison of model correlation (solid lines) with experimental carbon dioxide solubility in aqueous (a) 23.4% [8] and (b) 48.9% MDEA solutions [30].

Results and Discussion

Correlation of Carbon Dioxide Solubility

Fig. 1 compares the model correlation and experimental data points for carbon dioxide solubility in 15 wt%, 30 wt%, 45 wt% and 60 wt% aqueous solutions of MEA. It is observed that correlation gave satisfactory results. The model seems to overestimate the values at higher carbon dioxide solubility, which can be attributed to carbamate reversion to bicarbonate which is a significant process at gas loadings near 0.5. The values are slightly under predicted at lower loadings.

Fig. 2 presents a comparison between calculated and experimental values for carbon dioxide solubility in 20.6 wt% and 77.6 wt% aqueous DEA solutions. The predicted values show a similar pattern to MEA, where the model slightly over predicts at higher loadings. However, the onset of deviation is delayed in DEA. This is due to slow rate of carbamate reversion (as compared to MEA) at loadings of 0.5. Fig. 3 presents a comparison of

correlated values and the experimental data points for total carbon dioxide solubility in 23.4 wt% and 49 wt% aqueous solutions of MDEA. It can be seen that correlation is slightly over predicted at low temperatures but moderately under predicted with increase in temperature. This can be attributed to lower physical absorption of carbon dioxide at high temperatures, which was not adjusted due to absence of temperature based parameter in adjustment factor *f*.

Fig. 4 presents a comparison of correlated values and the experimental data points for total carbon dioxide solubility in 17.6 wt% and 42.9 wt% aqueous solutions of AMP. The model correlation is slightly over predicted at low temperatures. The model results are moderately over predicted with increase in temperature. However, the correlation is slightly under-correlated at pressures above 10kPA for all temperatures. This is attributed to the strong definition of regression parameter, *B* in the stated system. Fig. 5 represents the parity plots of carbon dioxide solubility in aqueous MEA, DEA, MDEA and AMP solutions. The parity of MEA and DEA solutions are evenly distributed among all the correlated carbon dioxide solubility values. However, the parity plots of MDEA and AMP based absorption systems show nominal deviation (maximum single point AARD is 17.6%) in the medium CO_2 solubility

values. The deviation in this region is attributed to the strong dependence of total carbon dioxide solubility on $[CO_2]_{physical}$ and the regression parameter D, especially in the low MDEA and AMP concentrations.

Correlation of Ionic Speciation

Fig. 6(a) compares the model results with the experimentally determined liquid phase ionic equilibria CO_2-DEA-H_2O system [23]. The model correlation is satisfactory and comparable to the rigorous and complex excess Gibbs energy model of Deshmukh and Mather [10]. However, the ease of prediction with the proposed model is highly promising. Fig. 6(b) shows the comparison of the correlated ionic profile of bicarbonate, protonated MDEA, free MDEA and total carbon dioxide dissolved for the proposed model and the Kent-Eisenberg (KE) model for carbon dioxide loaded aqueous MDEA solution. The predictions of both models are comparable for wide range of loadings. The proposed model enjoys the simplicity in calculations as compared to iterative set of equations involved in KE model. Since experimental ionic phase equilibria data for the discussed system is not available, both models could not be compared to experimental values of individual ionic species.
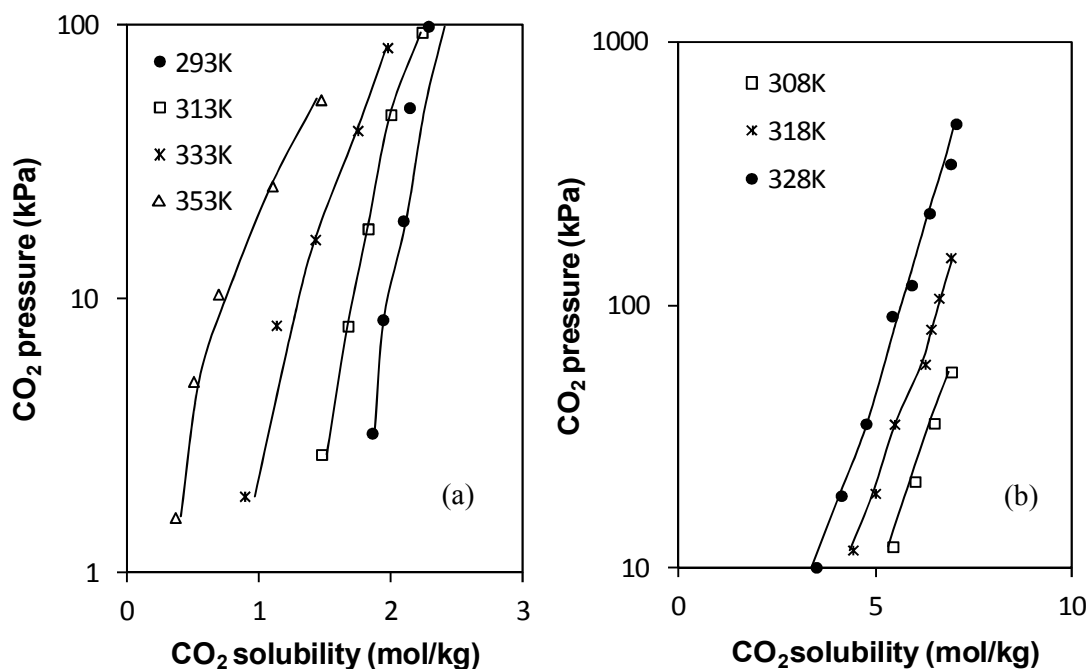

Fig. 4: Comparison of model correlation (solid lines) with experimental carbon dioxide solubility in aqueous (a) 17.6% [31] and (b) 42.9% AMP solutions [4].
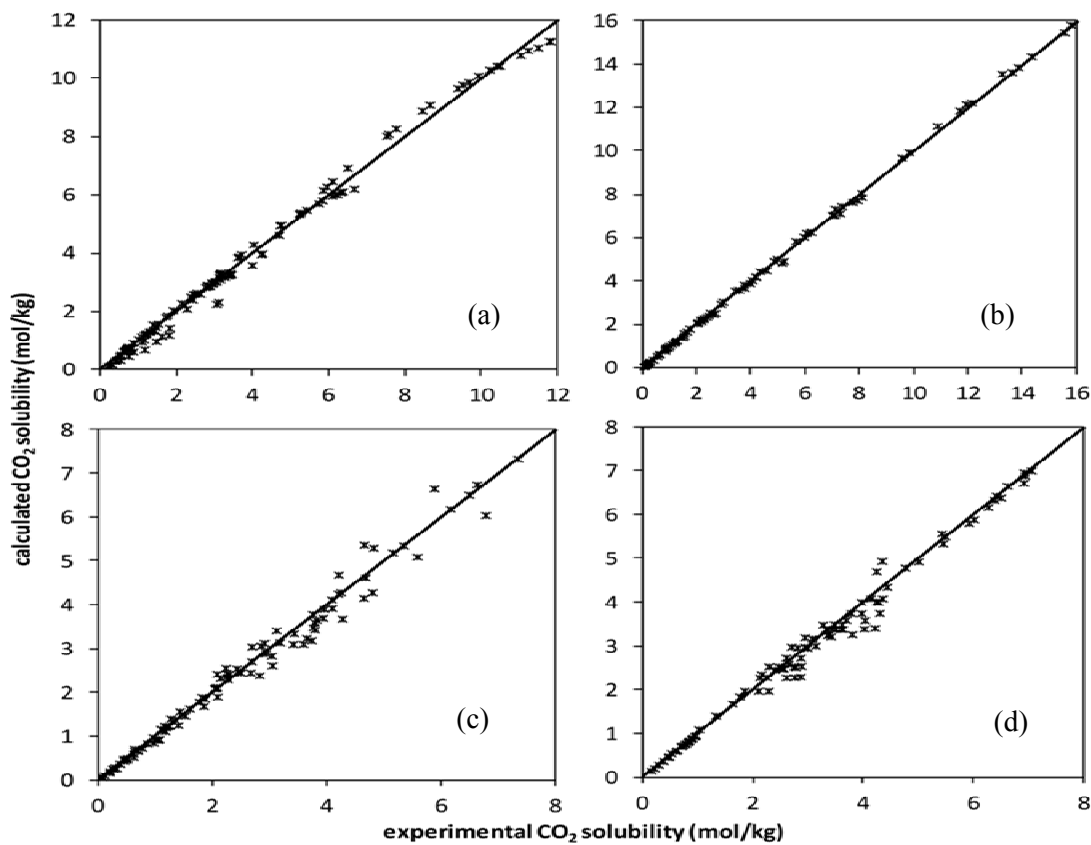
Fig. 5: Parity plots of calculated and experimental carbon dioxide solubility in aqueous (a) MEA, (b) DEA, (c) MDEA and (d) AMP solutions.
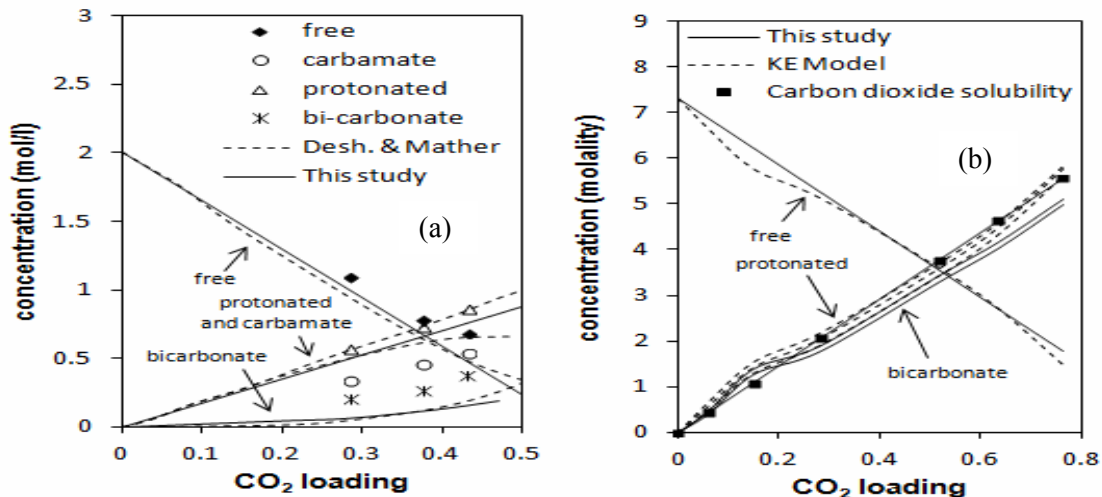

Fig. 6: Comparison of correlated ionic species (solid lines for proposed model and dotted line for Deshmukh and Mather [10]) and experimental ionic equilibria for (a) 20.6% DEA and (b) 46.5% MDEA solutions at 303.15 K. The dotted points show experimental data values. The proposed model assumes protonated and carbamate DEA as identical quantities in given loadings. Therefore, the prediction lines of proposed model for protonated DEA and carbamate DEA are identical.

Conclusions

Carbon dioxide solubilities and ionic speciation in aqueous solutions of MEA, DEA, MDEA and AMP have been correlated using a simple explicit approach. A single combined chemical reaction equilibrium equation has been developed. The model equation can be solved on a hand-held calculator. The formation of ionic species (bicarbonate, carbonate, hydrogen and alkanolamine based ions) has been taken into account. The parameters have been regressed to published carbon dioxide solubility data. The model can correlate carbon dioxide solubilities and ionic speciation for carbon dioxide loadings of 0.001 – 0.9 for MDEA and AMP solutions and 0.002 – 0.48 for MEA and DEA solutions, respectively. The model results are in good agreement with a variety of experimental data. The observed AARD values range between 7 – 10% with 516 selected data points. The proposed approach is easy in calculations and the results are comparable to rigorous thermodynamic approaches used in correlation of solubility and ionic equilibria of carbon dioxide based species.

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