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Solubility of CO_2 in Aqueous Blends of (Diethanolamine + 2-Amino-2-methyl-1-propanol) and (Diethanolamine + *N*-Methyldiethanolamine)

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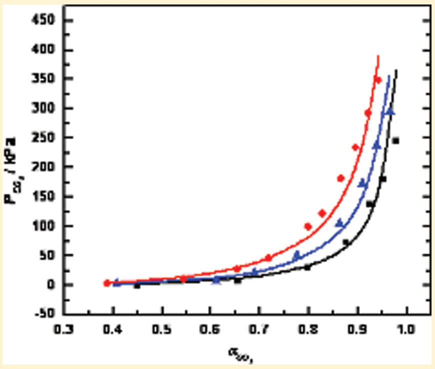
ABSTRACT: This work presents experimental data for the CO_2 solubility in aqueous blends of diethanolamine (DEA) + 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA) + *N*-methyldiethanolamine (MDEA) at temperatures of (303.1, 313.1, and 323.1) K and CO_2 pressure in the range of (1 to 350) kPa. Aqueous ternary mixtures of (DEA + AMP) and (DEA + MDEA) with the following compositions (0.06 mass fraction/0.571 $mol\cdot L^{-1}$ DEA + 0.24 mass fraction/2.692 $mol\cdot L^{-1}$ AMP), (0.09 mass fraction/0.856 $mol\cdot L^{-1}$ DEA + 0.21 mass fraction/2.356 $mol\cdot L^{-1}$ AMP), (0.12 mass fraction/1.141 $mol\cdot L^{-1}$ DEA + 0.18 mass fraction/2.019 $mol\cdot L^{-1}$ AMP), and (0.15 mass fraction/1.427 $mol\cdot L^{-1}$ DEA + 0.15 mass fraction/1.683 $mol\cdot L^{-1}$ AMP) and (0.06 mass fraction/0.571 $mol\cdot L^{-1}$ DEA + 0.24 mass fraction/2.014 $mol\cdot L^{-1}$ MDEA), (0.09 mass fraction/0.856 $mol\cdot L^{-1}$ DEA + 0.21 mass fraction/1.762 $mol\cdot L^{-1}$ MDEA), (0.12 mass fraction/1.141 $mol\cdot L^{-1}$ DEA + 0.18 mass fraction/1.511 $mol\cdot L^{-1}$ MDEA), and (0.15 mass fraction/1.427 $mol\cdot L^{-1}$ DEA + 0.15 mass fraction/1.259 $mol\cdot L^{-1}$ MDEA) were considered. The total alkanolamine mass fraction was held constant at 0.3. The solubility data produced were correlated within a thermodynamic framework using an extended Debye−Hückel theory of electrolytic solution and the virial equation of state.



■ INTRODUCTION

The removal of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from natural gas and refinery off gases is a very important industrial operation, which necessitates the application as well as promotion of a whole range of alkanolamines starting from monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP) and very recently piperazine (PZ), 2-piperidineethanol (2-PE), *N*-methyl-2-ethanolamine (MAE), and 2-(ethylamino)ethanol (EAE). By varying the relative composition of amines in their aqueous blends to exploit their individual merits, an optimum as well as energy efficient absorption system can be designed for a specific application. Specifically the use of sterically hindered amines in the aqueous blends of amines enhances the capacity and rate of absorption of acid gases with good stripping characteristics, reduced coabsorption capacity of hydrocarbons, and degradation resistance of the formulated solvent.

The evaluation of newer solvents having a high absorption capacity toward both acid gases and selectivity toward one of the acid gases, preventing undesirable products, for example, thermally stable salts or carbamates with minimum foaming, corrosion, and fouling problems have been the unremitted pursuits by the gas treating research community. It might be appropriate to mention some of the recent contributions in this regard. Rebolledo-Libreros and Trejo presented the solubility of carbon dioxide in an aqueous solution of 32.5 wt % (0.325 mass fraction) MDEA and 12.5 wt % (0.125 mass fraction) DEA with (4, 6, and 10) wt % (0.04, 0.06, and 0.10 mass fraction) AMP at (313.15, 343.15, and 393.15) K, over a range of pressure from (3 to 2000) kPa, using a chromatographic method for analysis of the liquid phase. They calculated enthalpy of solution of CO_2 from the experimental solubility data.[1] Rebolledo-Libreros and Trejo also presented the solubility of hydrogen sulfide in aqueous solutions of 32.5 wt % (0.325 mass fraction) MDEA and 12.5 wt % (0.125 mass fraction) DEA with (4, 6, and 10) wt % (0.04, 0.06, and 0.10 mass fraction) AMP, at (313.15, 343.15, and 393.15) K using a volumetric method for the analysis of the liquid phase, over a range of pressure from (2.5 to 1036) kPa.[2] Vapor−liquid equilibrium data of acid gases in such kinds of quaternary solutions for gas treating are rare in the open literature.

Recently PZ-activated solvents are being explored for sour gas treating. Yang et al. measured the equilibrium solubility of CO_2 in aqueous mixture containing AMP of concentrations of (2 and 3) $kmol\cdot m^{-3}$ (0.178 and 0.267 mass fraction) with PZ concentrations of (0.5, 1.0, and 1.5) $kmol\cdot m^{-3}$ (0.05, 0.10, and 0.15 mass fraction) at temperatures of (313.2, 333.2, and 353.2) K and pressures up to 152 kPa.[3] Dash et al. presented new experimental results for carbon dioxide solubility in aqueous PZ in the temperature range of (298 to 328) K and CO_2 partial pressure of about (0.1 to 1500) kPa. The concentrations of the aqueous PZ were in the range of about (0.2 to 4.5) M (0.02 to 0.45 mass fraction).[4]

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Another significant development using sterically hindered alkanolamines like MAE, EAE, and butylamino ethanolamine (BAE) is in progress for acid gas treating. Kumar and Kundu reported CO_2 solubility in MAE aqueous solutions of concentrations ((0.968, 1.574, 2.240, and 3.125) $mol \cdot kg^{-1}$ of solvent; 0.0676, 0.1052, 0.1427, and 0.1878 mass fraction) at temperatures of (303.1, 313.1, and 323.1) K in the CO_2 pressure range of (1 to 350) kPa.[5]Bougie and Iliuta measured and reported CO_2 solubility in aqueous mixtures of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) and PZ over a range of temperature from (288.15 to 333.15) K and for total amine concentrations up to 3.1 $kmol \cdot m^{-3}$ (0.37 mass fraction). The CO_2 partial pressure was kept within (0.21 to 2637) kPa using a vapor−liquid equilibrium (VLE) apparatus based on a static-analytic method.[6]

Vapor−liquid equilibrium, solvent vapor pressure, and kinetic data are not the only merits for a solvent formulation to consider it as a potential absorber; properties like corrosive property, degradation resistance, tendency of coabsorption of hydrocarbons, foaming characteristics, and cost effectiveness are favorable to establish that claim. The application of blended alkanolamines like aqueous DEA + AMP and DEA + MDEA in sour gas treating has been an area of focused research and development activities over almost one and half decades. The results of CO_2 solubility in DEA + AMP blends have been reported so far by Seo and Hong,[7] Murrieta-Guevara et al.,[8] Kundu and Bandyopadhyay,[9]and Park et al.[10]Seo and Hong reported the solubility of CO_2 in blends of (6 wt % (0.06 mass fraction) DEA + 24 wt % (0.24 mass fraction) AMP), (12 wt % (0.12 mass fraction) DEA + 18 wt % (0.18 mass fraction) AMP), and (18 wt % (0.18 mass fraction) DEA + 12 wt % (0.12 mass fraction) AMP) in the partial pressure range of (10 to 300) kPa and at temperatures of (313, 333, and 353) K.[7] Murrieta-Guevara et al. measured the CO_2 solubility in aqueous solutions with the following compositions of (25 wt % (0.25 mass fraction) DEA + 5 wt % (0.05 mass fraction) AMP) and (20 wt % (0.20 mass fraction) DEA + 10 wt % (0.10 mass fraction) AMP) in the temperature range of (313.15 to 373.15) K and in the CO_2 partial pressure range of (22 to 2600) kPa.[8] Kundu and Bandyopadhyay reported CO_2 solubility in aqueous blends with the following compositions of (1.5 wt % (0.015 mass fraction) DEA + 28.5 wt % (0.285 mass fraction) AMP), (3 wt % (0.03 mass fraction) DEA + 27 wt % (0.27 mass fraction) AMP), (4.5 wt % (0.045 mass fraction) DEA + 25.5 wt % (0.255 mass fraction) AMP), and (6 wt % (0.06 mass fraction) DEA + 24 wt % (0.24 mass fraction) AMP) at temperatures of (303, 313, and 323) K and in the CO_2 partial pressure range of (1 to 100) kPa.[9] Park et al. measured CO_2 solubility in aqueous solutions with the following blends of (20 wt % (0.20 mass fraction) DEA + 10 wt % (0.10 mass fraction) AMP) and (10 wt % (0.10 mass fraction) DEA + 20 wt % (0.20 mass fraction) AMP) at temperatures of (313, 333, and 353) K and in the CO_2 partial pressure range of (0.680 to 340) kPa.[10] The results of CO_2 solubility in aqueous DEA + MDEA blends have been reported so far by Austgen et al.,[11] Dawodu and Meisen,[12] Kundu and Bandyopadhyay[13] and Murrieta-Guevara et al.[8]Austgen et al. reported CO_2 solubility in (2.0 M (0.238 mass fraction) MDEA + 2.0 M (0.2103 mass fraction) DEA) aqueous solutions at (313 and 353) K over the CO_2 partial pressure range of (0.136 to 310) kPa.[11] Dawodu and Meisen reported the equilibrium solubility of CO_2 at temperatures of (343, 373, 393, 413, 433, and 453) K and in the CO_2 partial pressure range of (65 to 3200) kPa for (3.4 M (0.405 mass fraction) MDEA + 0.8 M (0.084 mass fraction) DEA) and (2.1 M (0.25 mass fraction) MDEA + 2.1 M (0.221 mass fraction) DEA) aqueous solutions.[12] Kundu and Bandyopadhyay reported CO_2 solubility in aqueous blends with the following compositions of (1.5 wt % (0.015 mass fraction) DEA + 28.5 wt % (0.285 mass fraction) MDEA), (3 wt % (0.03 mass fraction) DEA + 27 wt % (0.27 mass fraction) MDEA), and (4.5 wt % (0.045 mass fraction) DEA + 25.5 wt % (0.255 mass fraction) MDEA) at temperatures of (303, 313, and 323) K and in CO_2 partial pressure of (1 to 100) kPa.[13] Murrieta-Guevara et al. measured the solubility of CO_2 in 10 wt % (0.10 mass fraction) DEA + 15 wt % (0.15 mass fraction) MDEA, 10 wt % (0.10 mass fraction) DEA + 20 wt % (0.20 mass fraction) MDEA, 20 wt % (0.20 mass fraction) DEA + 10 wt % (0.10 mass fraction) MDEA, and 10 wt % (0.10 mass fraction) DEA + 35 wt % (0.35 mass fraction) MDEA aqueous solutions at (313.15 and 393.15) K.[8]

Reported CO_2 solubilities in aqueous blends of (DEA + AMP) and (DEA + MDEA) are not systematic as well as plentiful. In view of this, a systematic generation as well as an extension of the database on CO_2 solubility in the blends of (DEA + AMP + H_2O) and (DEA + MDEA + H_2O) at temperatures that included typically absorption temperatures of an absorption tower, (303.1, 313.1, and 323.1) K, were taken up. The generated data are potential because it determines the minimum recirculation rate through the absorber. It can also play an important role in rate-based models by defining the boundary conditions for the partial differential equations that describe mass transfer coupled with chemical reactions.

It is necessary to correlate the experimental data within a thermodynamic framework which provide a means to confidently interpolate between and extrapolate beyond the range of reported experimental data. The confidence that is placed in interpolation and extrapolation (prediction) with the model is dependent on both correctness of model formulation and the quality of the data used to fit the parameters of the model. It might not be inappropriate here to mention few contributions regarding correlation and prediction of CO_2 solubility, specifically in (DEA + AMP + H_2O) and (DEA + MDEA + H_2O) solutions. Austgen et al. utilized the non-random two-liquid (NRTL) theory to model acid gas (CO_2 and H_2S) VLE in aqueous MDEA and in MDEA + MEA and MDEA + DEA blends.[11,14] Li and Mather simplified the Clegg−Pitzer equations and applied them to model the system (CO_2 + MDEA + MEA + H_2O).[15] Jane and Li measured the solubility of mixed acid gases CO_2 and H_2S in aqueous blends of (DEA + AMP) and correlated their generated data with the model proposed by Deshmukh and Mather.[16,17] Kundu and Bandyopadhyay correlated the solubility of CO_2 into aqueous blends of (DEA + AMP) and (DEA + MDEA) with modified Clegg−Pitzer equations using simulated annealing as optimization technique for parameter estimation of the activity coefficient model.[9,13] Park et al. correlated the solubility of CO_2 into aqueous blend of (DEA + AMP) with modified Kent and Eisenberg approach.[10] In the present work, a rigorous thermodynamic model using extended Debye−Hückel theory of electrolytic solution with the virial equation of state was used to correlate and predict the CO_2 solubility in aqueous alkanolamine blends.

■ EXPERIMENTAL SECTION

Materials. 2-Amino-2-methyl-1-propanol (AMP), *N*-methyldiethanolamine (MDEA), and diethanolamine (DEA) were

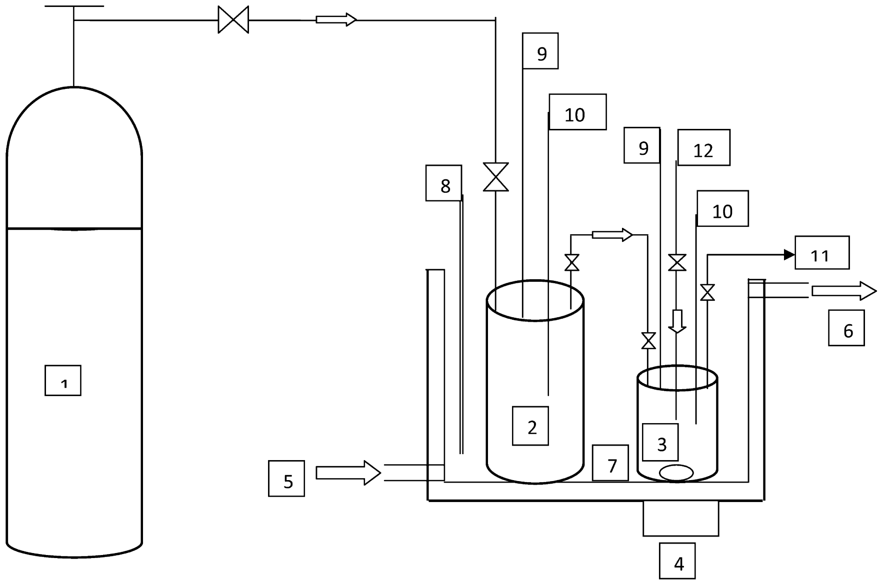

Figure 1. Schematic of experimental setup. 1, CO_2 cylinder; 2, buffer vessel; 3, VLE cell; 4, magnetic stirrer; 5, water from circulator; 6, water to circulator; 7, water bath; 8, Pt 100 temperature sensor; 9, pressure transducer; 10, temperature sensor; 11, vacuum pump; 12, buret.

supplied by E. Merck, Germany, and had a mol % purity >95.0, >98.0, and >98.0, respectively. Double-distilled water degassed by boiling was used for making the alkanolamine solutions. Alkanolamines may be distilled under vacuum to remove any possible traces of moisture and other impurities like CO_2 before they are used to prepare the solutions. In the present study, the prepared blended alkanolamine solutions were kept under vacuum for more than (10 to 20) min before commencement of the reaction in the VLE cell, so that the solutions exist under their own vapor pressure only. The mole L^{-1} (strengths) equivalent of requisite mass fraction of single alkanolamine solutions were determined by titration with standard HCl using a methyl orange indicator. Following the standard acid−base titration procedure, the normality of aqueous alkanolamine solutions was determined. The uncertainty in determining the composition sneaked in at transfers from pipet and buret. The estimated uncertainty in molarity was ± 1 % assuming the precise and perfect determination of end points of titrations. Methyl orange indicator used to determine end points undergoes a color change over a narrow range of pH (3.1 to 4.4) in comparison to other indicators like bromophenol blue (3.0 to 4.6) and bromocresol green (3.8 to 5.4). The standardized single alkanolamine solutions were used to prepare blended alkanolamine solutions. Pure carbon dioxide, obtained from Vadilal Gases Limited, India, had mole fraction of 0.9999.

Apparatus. The solubility of CO_2 in aqueous alkanolamine blends was measured in a stainless steel equilibrium cell. Figure 1 shows a schematic diagram of the apparatus. VLE measurements were done at pressures ranging from (1 to 350) kPa and at temperatures of (303.1, 313.1, and 323.1) K. The VLE apparatus consists of two stainless steel cylindrical tanks, namely, buffer vessel and vapor−liquid equilibrium cell of volumes (1480 and 780) mL, respectively, submerged in a water bath. The temperature of the water bath, hence, equilibrium cell and gas buffer is controlled within ± 0.2 K of the desired level with the help of a circulator temperature controller (Polyscience, model no. 9712) operated on an external mode, and the uncertainty in temperature measurement is ± 0.1 K. Precalibrated platinum sensors (Pt-100, Julabo) with a temperature indicator (Julabo TD300) are additionally used for measurement of temperatures in the equilibrium cell and gas buffer, and the uncertainty in temperature measurement is ± 0.1 K. A vacuum pump (INDVAC, model-IV-50) capable of creating 2 kPa pressure is attached to the buffer vessel through the VLE cell and is used to evacuate both the vessels before the commencement of the experiment. Pressure transducers in the range of (0 to 1724) and (0 to 689) kPa (PMP450, FUTEK) are attached to the buffer vessel and the equilibrium cell, respectively. The accuracy and nonrepeatability of each of the pressure transducers are ± 0.25 % and ± 0.1 % of the rated output, respectively. In the event of attainment of pressures equal to the maximum pressure limits measurable by the pressure transducers, the maximum combined uncertainty ($k = 2$) in the pressure measurements can reach up to ± 0.36 % (≅ ± 0.4 %) and ± 0.46 % (≅ ± 0.5 %) of the transducers' readings attached to the buffer vessel and the equilibrium cell, respectively. The VLE cell is equipped with a liquid phase stirrer (SPINOT, magnetic stirrer, Tarson).There are ball valves (Swagelok) controlling the transfer of gas from CO_2 cylinder to buffer vessel and from buffer vessel to VLE cell.

Procedure. For each set of runs, the buffer vessel and the VLE cell were allowed to reach in temperature equilibration with water bath undergoing constant water recirculation with the help of the circulator temperature controller. Air was evacuated by vacuum pump from both the vessels at a time by opening the valve connecting both the vessel. After evacuation, the buffer vessel was made isolated from VLE cell by closing the valve between them and was allowed to receive 1.5 to 2.5 times of the desired maximum CO_2 partial pressure (total pressure here) from pure CO_2 gas cylinder. A sample of 25 mL of freshly prepared mixed alkanolamine solution of the desired concentration was sucked into the VLE cell with the help of attached buret, and the cell was fully sealed. The maximum error in the transferred volume was estimated to be 0.05 mL. A vacuum was initially present in the VLE cell, and it was again evacuated for the second time. The VLE cell was kept under this condition for over (10 to 20) min duration so that the liquid existed under its own vapor pressure. This solution vapor pressure (p_v) was noted. The CO_2 gas from the buffer was then allowed to enter to the equilibrium cell, and after the transfer, the buffer vessel was temporarily isolated from the VLE cell with the help of the valve.

The amount of CO_2, hence, the moles of CO_2 being transferred from the buffer vessel, was calculated using the difference in pressure transducer reading attached to it. At the commencement of absorption in VLE cell, the liquid phase stirrer was kept on. The attainment of equilibrium in the VLE cell was ensured when there was no change in total pressure of the VLE cell for at least one hour while the temperature was maintained constant at its desired level. It took about 1 h to reach equilibrium for each run (one equilibrium point). The pressure transducer attached to the VLE cell was an indication of the total cell pressure (P_t). The equilibrium pressure (P_{CO_2}) was calculated by taking the difference of the total pressure of the cell, P_t, and vapor pressure (p_v)($P_{CO_2} = P_t - p_v$). The amount (moles) of CO_2 absorbed by the aqueous alkanolamine blends in the VLE cell was calculated by the difference in moles of CO_2 being transferred from the buffer vessel and moles of CO_2 present in the gas phase of the VLE cell at equilibrium pressure by taking into account the compressibility factor of the gas. The method of calculation adopted regarding the number of moles of CO_2 absorbed in the liquid phase was that of described by Park and Sandall (2001).[18] At that total equilibrium pressure, the CO_2 loading has been expressed as moles of CO_2 absorbed per moles of alkanolamine. The liquid-phase mole fraction of CO_2 at equilibrium was also calculated at each equilibrium point. The maximum combined uncertainty ($k = 2$) in CO_2 loading was found to be ± 3.0 % of the estimated loading. After the completion of one run, once again the valve between the buffer vessel and the VLE cell was reopened, and gas was transferred from buffer vessel to the VLE cell; the whole procedure was repeated for the second run to generate solubility data at a higher CO_2 pressure than the previous one.

To validate the present experimental setup, several VLE measurements were done in aqueous solutions of 0.3 mass fraction of DEA at 313.1 K. New data agree well with the literature data (Seo and Hong, 1996; Kundu, 2004[7,19]). The same experimental setup was used by the present authors to generate VLE data of CO_2 in aqueous solutions of MAE (Kumar and Kundu, 2011).[5] Figure 2 presents the comparison.

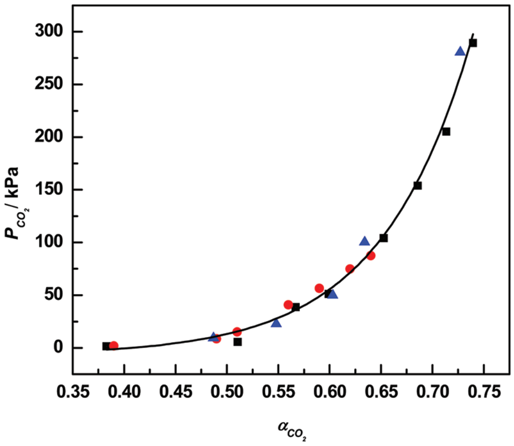

Figure 2. Comparison of solubility data for CO_2 (1) in aqueous solution of 0.30 mass fraction DEA (2) at T = 313.1 K. ○, Kundu;[19] △, Seo and Hong;[7] □, this work.

■ MODEL DEVELOPMENT

Chemical Equilibria. The following chemical equilibria are involved in the aqueous phase for the (CO_2 + DEA + AMP/MDEA + H_2O) system.

Ionization of water:

$$H_2O \overset{K_1}{\leftrightarrow} H^+ + OH^- \tag{1}$$

Hydration of carbon dioxide:

$$CO_2 + H_2O \overset{K_2}{\leftrightarrow} H^+ + HCO_3^- \tag{2}$$

Dissociation of bicarbonate:

$$HCO_3^- \overset{K'_3}{\longleftrightarrow} H^+ + CO_3^{-2} \tag{3}$$

Dissociation of protonated secondary amine (DEA):

$$RR'R''NH^+ \overset{K'_4}{\longleftrightarrow} H^+ + RR'R''N \tag{4}$$

Dissociation of protonated tertiary amine (MDEA):

$$RR'R'NH^+ \overset{K_5}{\leftrightarrow} H^+ + RR'R'N \tag{5}$$

Dissociation of carbamate:

$$RR'R''NCOO^- + H_2O \overset{K'_6}{\longleftrightarrow} HCO_3^- + RR'R''N \tag{6}$$

Hydration of AMP:

$$\begin{aligned} &H_2O + (C_2H_2(CH_3)_2OH)NH_2 \\ &\overset{K''_7}{\longleftrightarrow} OH^- + (C_2H_2(CH_3)_2OH)NH_3^+ \end{aligned} \tag{7}$$

$$\begin{aligned} AMPH^+ &\overset{K_8}{\longrightarrow} AMP + H^+ \\ &= RR'R'NH^+ \\ &\overset{K_8}{\leftrightarrow} H^+ + RR'R'N \end{aligned} \tag{8}$$

$$K_8 = \frac{K_1}{K''_7} \tag{9}$$

For DEA, R, R′, and R″ represent H, C_2H_4OH, and C_2H_4OH, respectively; for MDEA, R, R′, and R′ are CH_3, C_2H_4OH, and C_2H_4OH, respectively, and for AMP R, R′, and R′ are H, H, and $C_2H_2(CH_3)_2OH$, respectively. The equilibrium constant for deprotonation of AMP was obtained by mathematical manipulation of reactions 1 and 7, which resulted in reaction 8. K'_i is the mole fraction based equilibrium constant; K''_i is the equilibrium constant in molarity scale (kmol·m^{-3}), and K_i is the equilibrium constant in molality scale (mol of solute alkanolamine per kg water). The equilibrium constant for reaction 7 is on the molarity (kmol·m^{-3}) scale, and equilibrium constants for reaction 4 and 6 are mole fraction based which were converted to the molality scale to adapt in the model. The temperature-dependent equilibrium constants along with their literature sources are presented in Table 1.

Thermodynamic Framework. For the (CO_2 + DEA + AMP + H_2O)/(CO_2 + DEA + MDEA + H_2O) systems, the equilibrated liquid phase is assumed to contain three molecular species (H_2O, DEA, and AMP/MDEA) and five ionic species ($AMPH^+$/$MDEAH^+$, HCO_3^-, $DEAH^+$, $DEACOO^-$, and H_3O^+). Species like free molecular CO_2, OH^-, and CO_3^{2-} will have a little effect on the observed equilibria. Several previous researchers (Haji-Sulaiman et al.; Posey)[20,21] have observed that neglecting the concentrations

Table 1. Temperature Dependence of the Equilibrium Constants and Henry's Constant

$$\ln K_i/\text{mol.kg}^{-1} = C_1 + C_2/(T/K) + C_3 \ln T/K + C_4\, T/K \quad \text{where i=1, 2, 5}$$

$$\ln K'_i = C_1 + C_2/(T/K) + C_3 \ln T/K + C_4\, T/K \quad \text{where i=4, 6}$$

$$\ln K''_i/\text{kmol.m}^{-3} = C_1/(T/K) + C_2 \ln T/K + C_4 \quad \text{where i= 7}$$

$$\ln H_{CO_2}/\text{kg.atm.mol}^{-1} = C_1 + C_2/(T/K) + C_3 \ln T/K + C_4\, T/K$$

reaction	C_1	C_2	C_3	C_4	ref
2	235.482	−12092.1	−36.7816	0	*c*
4	−6.7936	5927.65	0	0	*a*
6	4.5416	−3417.34	0	0	*a*
5	−59.55	1709	8.01	0	*b*
7	−7261.78	−22.4773	0	142.586	*d*
1	−13445.9	−22.4773	0	140.932	*d*
H_{CO_2}	94.4914	−6789.04	−11.4519	−0.010454	*c*

[a] Austgen et al., 1989.[14] [b] Posey, 1996.[21] [c] Edwards et al., 1978. [d] Silkenbäumer et al., 1998.

of free molecular CO_2, and OH^- and CO_3^{-2} ions in the liquid phase in this system for CO_2 loading (moles of CO_2 per moles of alkanolamine) below 1.0 does not result in significant error in the VLE predictions. In our calculation of activity coefficients of the components in the aqueous phase, the activity coefficients of DEA, AMP/MDEA, H_2O, $DEAH^+$, $AMPH^+$/$MDEAH^+$, $DEACOO^-$, and HCO_3^- are included to account for the nonideality of the liquid phase. As the free molecular CO_2 concentration in the liquid phase is negligible below the loading of 1.0, the value of γ_{CO_2} will be close to unity following the unsymmetric normalization of activity coefficient. We can calculate molal concentrations (mol/kg solvent water) of species in liquid phase based on true molecular or ionic species.

Standard States. For developing the model, both AMP/MDEA and DEA are treated as solutes, and the only solvent considered is water. The standard state associated with solvent water is the pure liquid at the system temperature and pressure. The adopted standard state for ionic solutes is the ideal, infinitely dilute aqueous solution at the system temperature and pressure. The reference state chosen for molecular solute CO_2 is the ideal, infinitely dilute aqueous solution at the system temperature and pressure.

Vapor−Liquid Equilibria. We have assumed that the amine is nonvolatile (relative to the other molecular species), an assumption that can be easily relaxed if necessary. It is assumed a physical solubility (Henry's law) relation for the (noncondensable) acid gases. Thus, the following iso-fugacity relation is applicable:

$$\varphi_{CO_2} P_{CO_2} = \gamma_{CO_2} m_{CO_2} H_{CO_2} \tag{10}$$

where φ_{CO_2} is the fugacity coefficient of CO_2, H_{CO_2} is a Henry's constant for CO_2 in pure water, and P_{CO_2} is the equilibrium partial pressure of CO_2. The Henry's constant was taken from literature and presented in Table 1. The vapor phase fugacity coefficient was calculated using the virial equation of state.

Thermodynamic Expression of Equilibrium Partial Pressure. From the aforesaid chemical reaction equilibria, mathematically, the corresponding equilibrium constants (converted in molality scale) are defined in terms of activity coefficients, γ, and molalities, m (mol·kg^{-1} solvent water), of the species present in the equilibriated liquid phase.

$$K_1 = \gamma_{H^+} m_{H^+} \gamma_{OH^-} m_{OH^-} \tag{11}$$

$$K_2 = \frac{\gamma_{H^+} m_{H^+} \gamma_{HCO_3^-} m_{HCO_3^-}}{\gamma_{CO_2} m_{CO_2}} \tag{12}$$

$$K_3 = \frac{\gamma_{H^+} m_{H^+} \gamma_{CO_3^{2-}} m_{CO_3^{2-}}}{\gamma_{HCO_3^-} m_{HCO_3^-}} \tag{13}$$

$$K_4 = \frac{\gamma_{H^+} m_{H^+} \gamma_{RR'R''N} m_{RR'R''N}}{\gamma_{RR'R''H^+} m_{RR'R''H^+}} \tag{14}$$

$$K_5 = K_8 = \frac{\gamma_{H^+} m_{H^+} \gamma_{RR'R'N} m_{RR'R'N}}{\gamma_{RR'R'NH^+} m_{RR'R'NH^+}} \tag{15}$$

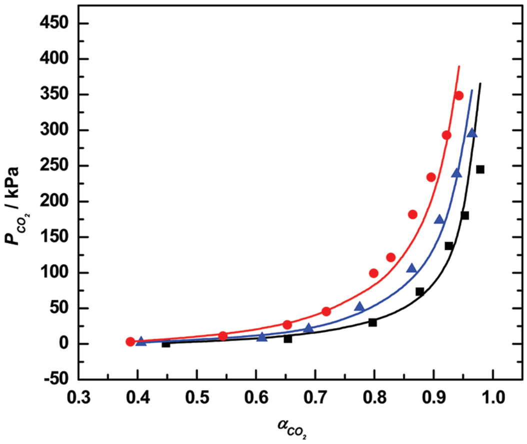

Figure 3. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.06 DEA (2) + 0.24 AMP (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

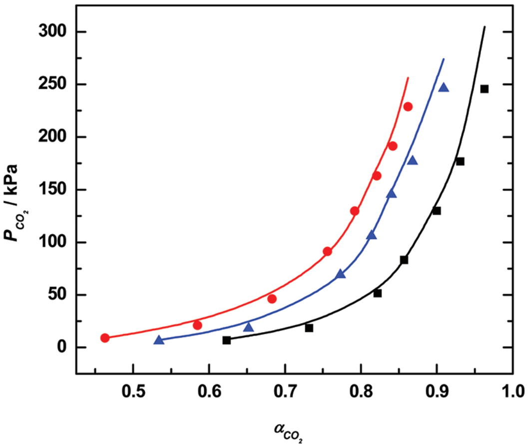

Figure 4. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.09 DEA (2) + 0.21 AMP (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

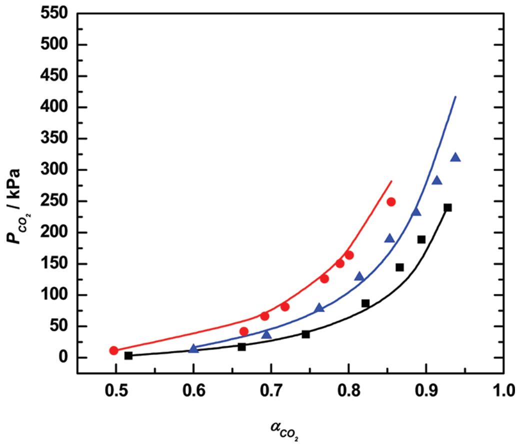

Figure 5. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.12 DEA (2) + 0.18 AMP (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

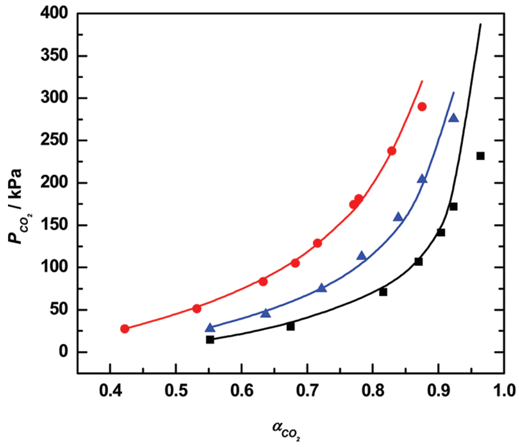

Figure 7. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.06 DEA (2) + 0.24 MDEA (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

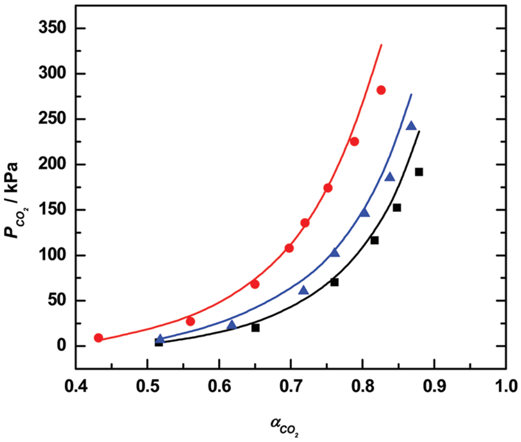

Figure 6. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.15 DEA (2) + 0.15 AMP (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

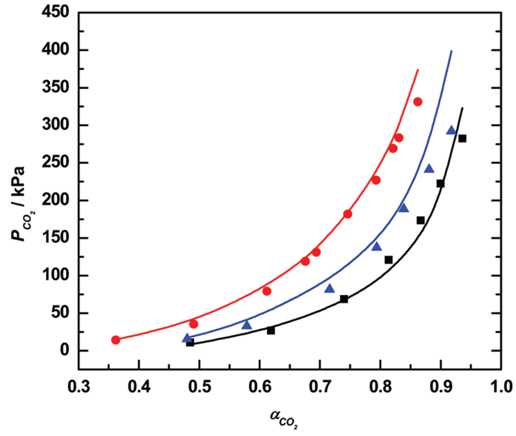

Figure 8. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.09 DEA (2) + 0.21 MDEA (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

$$K_6 = \frac{\gamma_{HCO_3^-} m_{HCO_3^-} \gamma_{RR'R''N} m_{RR'R''N}}{\gamma_{RR'R''NCOO^-} m_{RR'R''NCOO^-}} \tag{16}$$

The following balance equations for the reacting species can be formed:

Total amine balance:

$$m_1 = [RR'R''N] + [RR'R''NH^+] + [RR'R''NCOO^-] \tag{17}$$

$$m_2 = [RR'R'N] + [RR'R'NH^+] \tag{18}$$

Carbon dioxide balance:

$$(m_1 + m_2)\alpha = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RR'R''NCOO^-] \tag{19}$$

Equation of electroneutrality:

$$[H^+] + [RR'R''NH^+] + [RR'R'NH^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [RR'R''NCOO^-] \tag{20}$$

where α has been expressed as moles of CO_2 per moles of alkanolamine. Putting the value of $\gamma_{CO_2} m_{CO_2}$ from eq 12 into eq 10, the equation will be

$$\varphi_{CO_2} P_{CO_2} = \frac{\gamma_{H^+} m_{H^+} \gamma_{HCO_3^-} m_{HCO_3^-}}{K'_2} \cdot H_{CO_2} \tag{21}$$

Taking the value of $\gamma_{H^+} m_{H^+}$ from eqs 14 and 15 and $(\gamma_{HCO_3^-} m_{HCO_3^-})$ from eq 16 and substituting them into eq 21, the following relation results,

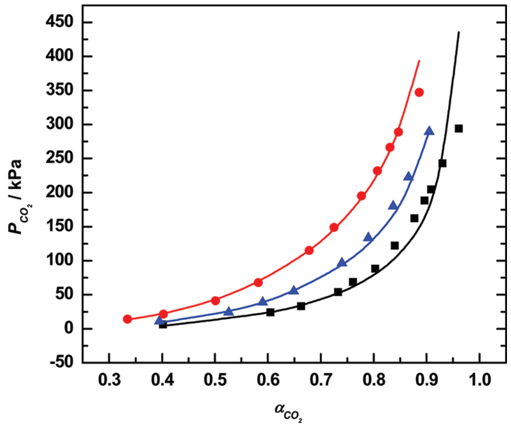

Figure 9. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.12 DEA (2) + 0.18 MDEA (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

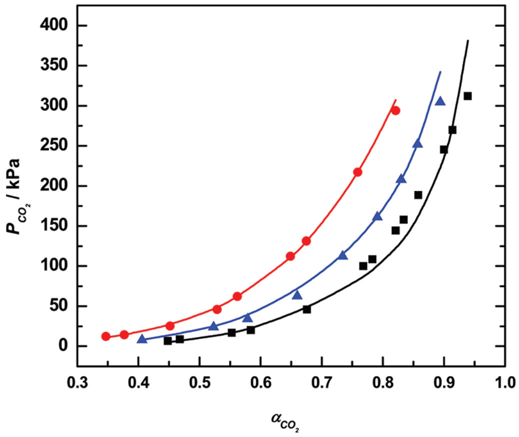

Figure 10. Solubility of CO_2 (1) in aqueous alkanolamine solution of mass fraction (0.15 DEA (2) + 0.15 MDEA (3)) at T = (303.1 to 323.1) K. □, 303.1 K; △, 313.1 K; ○, 323.1 K; and —, correlated data.

$$P_{CO_2} = \frac{H_{CO_2}}{\varphi_{CO_2}}\left(K_4 \frac{\gamma_{RR'R''H^+} m_{RR'R''H^+}}{\gamma_{RR'R''N} m_{RR'R''N}} + K_5 \frac{\gamma_{RR'R'H^+} m_{RR'R'H^+}}{\gamma_{RR'R'N} m_{RR'R'N}}\right) \cdot \left(\frac{K_6}{K_2} \frac{\gamma_{RR'R''NCOO^-} m_{RR'R''NCOO^-}}{\gamma_{RR'R''N} m_{RR'R''N}}\right) \tag{22}$$

The equilibrium concentrations of $m_{RR'R''H^+}$, $m_{RR'R''N}$, $m_{RR'R'NH^+}$, $m_{RR'R'N}$, $m_{RR'R''NCOO^-}$, and $m_{HCO_3^-}$ (mol·kg^{-1} solvent water) can be calculated rearranging the eqs 16 to 20 mathematically, which are as follows:

$$m_{RR'R''N} = m_1 - m_1\alpha - z \tag{23}$$

$$m_{RR'R'N} = m_2 - m_2\alpha \tag{24}$$

$$m_{RR'R''H^+} = m_1\alpha \tag{25}$$

$$m_{RR'R'H^+} = m_2\alpha \tag{26}$$

$$m_{RR'R''NCOO^-} = z \tag{27}$$

$$m_{HCO_3^-} = (m_1 + m_2)\alpha - z \tag{28}$$

where

$$z = [(K'_6 + m_1) - [(K'_6 + m_1)^2 - 4m_1^2\alpha(1 - \alpha)]^{1/2}]/2 \tag{29}$$

where α has been expressed as moles of CO_2 per moles of alkanolamine in eqs 23 to 29.

Activity Coefficient Model. The activity coefficient model consists of the Debye–Hückel term, which is one of the dominant terms in the expression for the activity coefficients in dilute solution, accounts for electrostatic, nonspecific long-range interactions. At higher concentrations, short-range, nonelectrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye–Hückel expression. The mathematical description of the two basic assumptions in the specific ion interaction theory is as follows:

$$\ln \gamma_i = -\frac{AZ_i^2 I^{0.5}}{1 + I^{0.5}} + 2\sum_j \beta_{ij} m_j \tag{30}$$

Here, A is the Debye–Hückel limiting slope (0.509 at 25 °C in water), and I is the ionic strength, defined as

$$I = \frac{1}{2}\sum_i m_i Z_i^2 \tag{31}$$

Here, Z is the charge number on the ion, β_{ij} (kg·mol^{-1}) represent the net effect of various short-range two-body forces between different molecular and ionic solutes. The summation in the second term of eq 30 is taken over all solute pairs but excludes interactions between solutes and the solvent, water. Physically, the first term on the right represents the contribution of electrostatic forces; the second term represents short-range van der Waals forces.

Calculation of Fugacity Coefficient. The fugacity coefficients were calculated using the virial equation of state. The fugacity coefficient of an acid gas in the gaseous mixture was approximated by the value of the fugacity coefficient of the acid gas (total CO_2 pressure here) at its partial pressure.

$$\ln \varphi_{CO_2} = \frac{B_{ii}}{RT}\int_0^P dP \tag{32}$$

or,

$$\ln \varphi_{CO_2} = \frac{B_{ii}P}{RT} \tag{33}$$

B_{ii} corresponds to interactions between pairs of molecules and can be calculated from virial equation of state.

$$\ln \varphi_{CO_2} = \frac{B_{ii}P_C P_R}{RT_C T_R} \tag{34}$$

$$\ln \varphi_{CO_2} = (B_1 + \omega B_2)\frac{P_R}{T_R} \tag{35}$$

where

$$B_1 = 0.083 - \frac{0.422}{T_R^{\ 1.6}} \tag{36}$$

$$B_2 = 0.139 - \frac{0.172}{T_R^{\ 4.2}} \tag{37}$$

Here, P_R and P_C are reduced and critical pressure; T_R and T_C are reduced and critical temperature, and ω is the acentric factor it has been taken to be 0.239 for CO_2. The values considered for P_C and T_C are 73.87 bar and 304.2 K, respectively. φ_{CO_2}, thus calculated, was used in eq 22.

■ METHOD OF SOLUTION

In this work the solubility data of CO_2 in aqueous blended alkanolamine solutions of various compositions, in a wide range of CO_2 pressure and temperatures below a CO_2 loading of 1.0 mol CO_2/mol amine, have been used to estimate the interaction parameters by regression analysis.

The objective function used for optimization is presented by eq 38

$$F = \sum \left| \frac{\{(P_{CO_2})_{cal} - (P_{CO_2})_{exp}\}}{\{(P_{CO_2})_{cal}(P_{CO_2})_{exp}\}} \right| \tag{38}$$

Owing to the presence of multiple solutions some approaches were unable to obtain the global solution for the parameter estimation problem because they could not jump over the local minima. A constrained optimization function using quasi-Newton and the sequential quadratic programming (SQP) method from MATLAB was used for minimization of the proposed objective function with variable bounds.

■ RESULTS AND DISCUSSION

The solubility of CO_2 in (DEA + AMP + H_2O) and (DEA + MDEA + H_2O) systems are presented in Tables 2 and 3, respectively. It is evident from Tables 2 and 3 that, at a fixed

Table 2. Solubility of CO_2 (1) in Aqueous (DEA (2) + AMP (3)) Solutions (Total Amine Mass Fraction = 0.3)[a]

DEA (2) + AMP (3)	T = 303.1 K			T = 313.1 K			T = 323.1 K		
mass fraction	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}
0.06 + 0.24	1.021	0.448	0.035	1.987	0.406	0.031	3.007	0.388	0.030
	6.996	0.654	0.050	8.298	0.610	0.047	11.01	0.544	0.042
	29.78	0.797	0.060	20.91	0.689	0.053	26.79	0.653	0.050
	73.48	0.877	0.066	51.20	0.775	0.061	45.32	0.719	0.055
	137.4	0.926	0.070	105.1	0.863	0.064	99.11	0.799	0.061
	180.0	0.953	0.071	173.6	0.910	0.068	121.1	0.828	0.063
	244.9	0.979	0.073	238.7	0.939	0.070	181.5	0.865	0.065
				295.0	0.965	0.072	234.1	0.896	0.067
				354.8	0.989	0.074	293.0	0.922	0.069
							348.6	0.943	0.071
0.09 + 0.21	6.695	0.623	0.047	6.038	0.534	0.040	8.987	0.463	0.035
	18.41	0.732	0.055	18.01	0.652	0.049	21.01	0.585	0.044
	51.31	0.822	0.061	69.11	0.773	0.057	46.02	0.683	0.051
	83.08	0.857	0.063	106.1	0.814	0.060	91.08	0.756	0.056
	129.8	0.900	0.066	145.4	0.840	0.062	129.5	0.792	0.059
	176.8	0.931	0.068	176.9	0.868	0.064	163.2	0.821	0.061
	245.6	0.963	0.071	246.1	0.909	0.067	191.3	0.842	0.062
							228.7	0.862	0.064
0.12 + 0.18	3.013	0.516	0.039	12.56	0.600	0.045	11.01	0.497	0.047
	17.01	0.662	0.049	35.31	0.694	0.052	41.63	0.665	0.050
	37.02	0.745	0.056	78.58	0.762	0.056	66.01	0.692	0.052
	86.51	0.822	0.061	128.6	0.814	0.060	81.00	0.718	0.055
	144.1	0.866	0.064	189.2	0.853	0.063	125.9	0.769	0.057
	188.6	0.894	0.065	232.0	0.887	0.065	150.2	0.789	0.058
	239.7	0.928	0.068	281.9	0.914	0.067	163.7	0.801	0.061
				318.7	0.938	0.069	248.9	0.855	0.062
0.15 + 0.15	4.021	0.516	0.037	6.795	0.518	0.038	8.998	0.432	0.032
	20.00	0.651	0.047	22.63	0.618	0.047	27.01	0.560	0.041
	70.11	0.761	0.055	60.45	0.718	0.053	68.21	0.650	0.047
	116.3	0.817	0.058	102.0	0.761	0.056	107.8	0.698	0.050
	152.3	0.848	0.060	146.0	0.803	0.060	135.6	0.72	0.052
	191.8	0.879	0.062	185.3	0.838	0.061	174.3	0.752	0.054
				241.8	0.868	0.063	225.2	0.789	0.055
							282.0	0.826	0.058

[a] α_{CO_2} = loading of CO_2 = moles of CO_2 per moles of alkanolamine, x_{CO_2} = CO_2 mole fraction in the equilibrated liquid phase.

Table 3. Solubility of CO_2 (1) in Aqueous (DEA (2) + MDEA (3)) Solutions (Total Amine Mass Fraction = 0.3)[a]

DEA (2) + MDEA (3)	T = 303.1 K			T = 313.1 K			T = 323.1 K		
mass fraction	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}	P_{CO_2}/kPa	α_{CO_2}	x_{CO_2}
0.06 + 0.24	14.79	0.552	0.038	27.58	0.552	0.033	27.56	0.422	0.025
	30.12	0.675	0.041	44.94	0.637	0.038	51.11	0.532	0.032
	70.89	0.816	0.049	74.70	0.722	0.043	83.30	0.633	0.037
	106.7	0.870	0.052	112.9	0.783	0.046	104.9	0.682	0.040
	141.2	0.904	0.054	158.7	0.839	0.049	128.7	0.716	0.041
	171.9	0.923	0.056	203.9	0.875	0.051	174.3	0.771	0.045
	231.8	0.964	0.057	275.8	0.923	0.053	181.2	0.779	0.046
							237.6	0.829	0.048
							290.1	0.875	0.052
0.09 + 0.21	6.496	0.402	0.025	10.89	0.395	0.024	14.03	0.335	0.021
	23.86	0.605	0.037	24.05	0.526	0.032	21.30	0.403	0.025
	32.83	0.663	0.040	38.92	0.590	0.036	41.08	0.501	0.030
	53.91	0.733	0.044	55.11	0.649	0.039	67.47	0.582	0.035
	68.54	0.761	0.045	96.64	0.740	0.044	114.9	0.678	0.040
	88.38	0.803	0.048	133.4	0.790	0.047	148.8	0.725	0.043
	122.2	0.840	0.050	180.2	0.837	0.050	195.0	0.777	0.046
	162.1	0.877	0.052	222.7	0.866	0.051	232.0	0.807	0.048
	188.2	0.896	0.053	289.5	0.905	0.054	266.3	0.831	0.049
	204.7	0.909	0.055				288.9	0.847	0.050
	242.8	0.930	0.056				346.9	0.886	0.053
	294.0	0.961	0.058						
0.12 + 0.18	10.81	0.485	0.030	15.89	0.480	0.029	14.07	0.362	0.023
	26.89	0.619	0.038	32.88	0.579	0.035	35.29	0.491	0.030
	68.80	0.740	0.045	81.51	0.716	0.043	79.12	0.612	0.038
	120.7	0.814	0.049	137.4	0.794	0.048	119.0	0.676	0.040
	173.5	0.867	0.052	188.7	0.839	0.050	131.1	0.694	0.042
	222.4	0.900	0.054	241.0	0.881	0.053	181.8	0.746	0.045
	282.3	0.936	0.056	292.1	0.918	0.055	227.1	0.793	0.048
							269.1	0.821	0.049
							283.3	0.831	0.050
							331.1	0.862	0.052
0.15 + 0.15	6.489	0.448	0.028	8.014	0.406	0.024	11.98	0.347	0.022
	8.632	0.468	0.029	23.79	0.523	0.032	14.21	0.377	0.024
	16.91	0.553	0.034	33.91	0.579	0.036	25.09	0.452	0.028
	20.20	0.584	0.036	62.49	0.660	0.041	45.92	0.529	0.033
	45.82	0.676	0.042	112.0	0.734	0.045	62.02	0.562	0.035
	100.0	0.768	0.047	161.0	0.791	0.047	112.0	0.649	0.040
	108.4	0.783	0.048	208.0	0.830	0.051	131.2	0.675	0.042
	144.3	0.821	0.050	251.9	0.857	0.052	217.0	0.759	0.046
	157.8	0.834	0.051	304.5	0.894	0.054	293.8	0.821	0.050
	188.7	0.858	0.052						
	245.3	0.900	0.054						
	269.8	0.914	0.055						
	312.0	0.939	0.057						

[a] α_{CO_2} = loading of CO_2 = moles of CO_2 per moles of alkanolamine, x_{CO_2} = CO_2 mole fraction in the equilibrated liquid phase.

temperature and an increase in mass fraction of DEA in the alkanolamine blends, there is a decrease in the solution CO_2 loading capacity. For any constant relative compositions in (DEA + AMP + H_2O) and (DEA + MDEA + H_2O) blends and CO_2 pressure, there is a decrease in solution CO_2 loading capacity with increasing temperature. The interaction parameters of the activity coefficient model for (CO_2 + DEA + AMP + H_2O) and (CO_2 + DEA + MDEA + H_2O) systems were obtained by regression analysis using the ternary solubility data generated in this work. Twelve numbers of interaction parameters (β_{ij} (kg·mol^{-1})) for each system were regressed with overall average correlation deviations in CO_2 partial pressure (with respect to the experimentally generated CO_2 pressure) by 5.3 % and 8.0 %, respectively, for (CO_2 + DEA + AMP + H_2O) and (CO_2 + DEA + MDEA + H_2O) systems. The resulted interaction parameters for the aforesaid systems are listed in Tables 4 and 5, respectively.

Figures 3 to 6 and 7 to 10 show the comparison between the correlated and the experimental solubility data of CO_2 in aqueous ternary mixtures of (DEA (2) + AMP (3)) and (DEA (2) + MDEA (3)), respectively, with various relative amine compositions. The figures reveal an acquiescent resemblance between the experimental and the correlated solubility, especially for aqueous (DEA (2) + MDEA (3)) blends.

Table 4. Interaction Parameters of the (CO_2–DEA–AMP–H_2O) System

binary pair of the (CO_2 + DEA + AMP + H_2O) system	$kg \cdot mol^{-1}$	AAD/% correlation
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R''NH^{+}})$	−2.228221	5.3
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R''N})$	−0.948782	
$\beta(\mathrm{RR'R''NH^{+}{-}HCO_3^{-}})$	−2.044120	
$\beta(\mathrm{RR'R''N{-}RR'R''NH^{+}})$	−1.235838	
$\beta(\mathrm{RR'R''N{-}HCO_3^{-}})$	−0.793460	
$\beta(\mathrm{RR'R''NH^{+}{-}RR'R'N})$	−0.647058	
$\beta(\mathrm{RR'R'NH^{+}{-}HCO_3^{-}})$	0.117060	
$\beta(\mathrm{RR'R'N{-}HCO_3^{-}})$	0.451332	
$\beta(\mathrm{RR'R'NCOO^{-}{-}RR'R'NH^{+}})$	−0.681037	
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R'N})$	−1.92113	
$\beta(\mathrm{RR'R''NH^{+}{-}RR'R'N})$	−0.336185	
$\beta(\mathrm{RR'R''N{-}RR'R'NH^{+}})$	0.274220	

Table 5. Interaction Parameters of the (CO_2–DEA–MDEA–H_2O) System

binary pair of (CO_2 + DEA + MDEA + H_2O) system	$kg \cdot mol^{-1}$	AAD[a]/% correlation
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R'NH^{+}})$	−0.841042	8.0
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R'N})$	0.293588	
$\beta(\mathrm{RR'R'NH^{+}{-}HCO_3^{-}})$	1.764229	
$\beta(\mathrm{RR'R''N{-}RR'R'NH^{+}})$	−0.761452	
$\beta(\mathrm{RR'R'N{-}HCO_3^{-}})$	1.301074	
$\beta(\mathrm{RR'R'NH^{+}{-}RR'R'N})$	0.681454	
$\beta(\mathrm{RR'R''NH^{+}{-}HCO_3^{-}})$	−0.028994	
$\beta(\mathrm{RR'R''N{-}HCO_3^{-}})$	0.048992	
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R''NH^{+}})$	0.511067	
$\beta(\mathrm{RR'R''NCOO^{-}{-}RR'R''N})$	0.464867	
$\beta(\mathrm{RR'R''NH^{+}{-}RR'R'N})$	0.512859	
$\beta(\mathrm{RR'R''N{-}RR'R'NH^{+}})$	−0.329676	

[a] AAD/% = $[\sum_n |(P_{CO_2,cal} - P_{CO_2,exp})| / P_{CO_2,exp}]/n \cdot 100$.

CONCLUSIONS

The alkanolamine blends of (DEA + AMP/MDEA) were used to generate the systematic CO_2 solubility data at temperatures of (303.1, 313.1 ,and 323.1) K and in the CO_2 pressure range of (1 to 350) kPa. The rigorous thermodynamic model developed in this work used two types of equilibria: phase equilibria and chemical reaction equilibria. The vapor-phase nonideality was taken care of in terms of the fugacity coefficient calculated using the virial equation of state. The extended Debye–Hückel theory of electrolytic solution was used to address the liquid phase non-ideality. The rigorous model developed in this work was a model with less computational rigor than any other rigorous thermodynamic model which is being used presently for predicting VLE of acid gases over alkanolamine blends. For (CO_2 + DEA + AMP + H_2O) and (CO_2 + DEA + MDEA + H_2O) systems, the correlated and experimental CO_2 pressures were in good agreement.

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