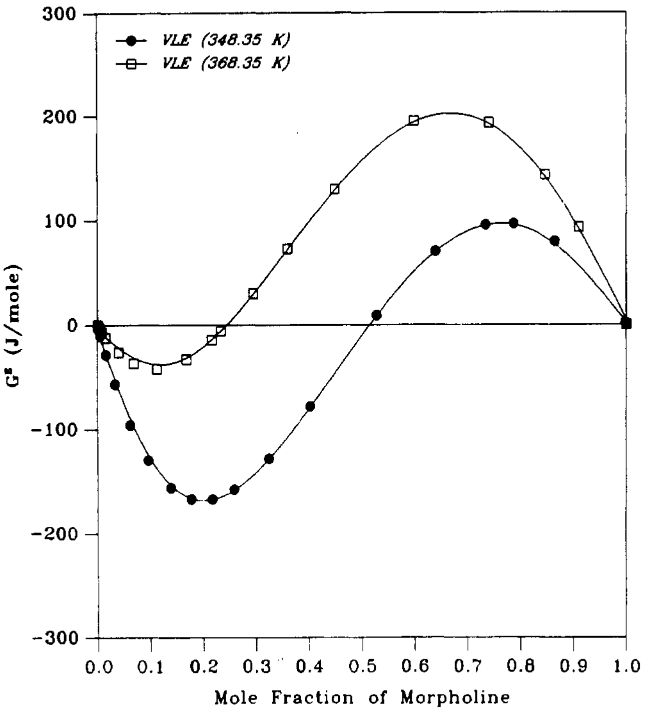

Figure 5. Molar excess Gibbs free energies, G^E, for the morpholine (1) + water (2) system. The points are generated from experimental VLE measurements, and the lines result from the three-constant Legendre polynomial expansion with $a_1 = -0.074\,29$, $a_2 = 0.474\,39$, and $a_3 = -0.122\,24$ at temperature $T = 348.35$ K and with $a_1 = 0.155\,80$, $a_2 = 0.327\,62$, and $a_3 = -0.100\,76$ at temperature $T = 368.35$ K.

The predictive UNIFAC model with parameters reported in the literature (*16*) results in poor predictions for all the mixtures studied here. This confirms our suspicion and the findings of Tine and Kehiaian (*17*) that the cyclic secondary amine group in pyrrolidine and morpholine have to be considered a different functional group from the noncyclic secondary amine group in future improvements of the UNIFAC model.

Registry No. BuOH, 71-36-3; morpholine, 110-91-8; cyclooctane, 292-64-8; octane, 111-65-9.

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Solubility of CO_2 in 2-Amino-2-methyl-1-propanol Solutions

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The solubility of carbon dioxide in 2 and 3 M solutions of 2-amino-2-methyl-1-propanol (AMP) was determined at 20, 40, 60, and 80 °C and for CO_2 partial pressures ranging from approximately 1 to 100 kPa. The results were interpreted with a modified Kent–Eisenberg model, which predicted the present and previous experimental results well. The absorption capacities of AMP and monoethanolamine (MEA) solutions are also compared.

Introduction

The separation of CO_2 from gas mixtures is an important step in petroleum refining, natural gas processing, and petrochemicals manufacture (*1*). Although numerous separation processes have been developed, the regenerative processes based on aqueous amine solutions have achieved the widest commercial acceptance (*2*). Recently, so-called "sterically hindered amines" have been introduced and are claimed to excel over conventional amines in terms of CO_2 absorption capacity, degradation resistance, and selectivity (*3*, *4*). Although knowledge of the CO_2 solubility is essential for process design, very little information has been reported in the open literature even for 2-amino-2-methyl-1-propanol, or "AMP", which is one of the more widely used sterically hindered amines. Sartori and Savage (*3*) reported the CO_2 solubility in 3 M AMP solutions at 40 and 120 °C. Roberts and Mather (*5*) provided CO_2 and H_2S solubility data for 2 M AMP solutions at 40 and 100 °C, and, more recently, Teng and Mather (*6*) have examined the dissolution of the same gases in 3.43 M AMP solutions at 50 °C.

The principal objective of this study is to acquire solubility data for CO_2 in 2 and 3 M AMP solutions at temperatures ranging from 20 to 80 °C since these values cover the typical operating ranges of absorbers. The present and previous data are subsequently interpreted with a modified Kent–Eisenberg model (*7*). The performance of AMP is also compared with that of monoethanolamine (MEA), which is a primary, conventional amine.

Experimental Apparatus and Procedure

The apparatus and procedures used in this study were similar to those described by Muhlbauer and Monaghan (*8*). Gas

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mixtures of the desired concentration were formed by metering streams of pure CO_2 and N_2 through precision rotameters. The mixture was then bubbled (at a flow rate of approximately 500 mL/min) through a gas disperser into a vessel filled with 50 mL of a NaCl solution, which had a water vapor pressure identical with that of the AMP solution under examination. The gas mixture was then sparged into an equilibrium vessel containing 50 mL of aqueous AMP solution. Both vessels were placed in a constant-temperature bath controlled to within ±0.5 °C. The CO_2 dissolution was followed by taking small samples of the AMP solution periodically; 4–8 h were usually required to reach equilibrium. Three AMP samples were then taken and analyzed for their amine concentration and CO_2 loading. The AMP concentrations were determined by titration with standard 1 M HCl solutions to the methyl orange end point. The CO_2 loadings were found by the standard AOAC method (*9*); i.e. the samples were treated with 2 M HCl, and the released CO_2 was measured with a precision gas burette.

Predictive Model for CO_2 Solubility in AMP Solutions

A model of the type proposed by Kent and Eisenberg (*7*) was chosen because it is based on the fundamental theory of Danckwerts and McNeil (*10*) and because it had given good performance for predicting acid gas solubilities in alkanolamine solutions.

The chemical equilibrium in systems comprised of CO_2, primary amines, and water is governed by the following equations:

$$RNH_3^+ = H^+ + RNH_2 \tag{1}$$

$$RNHCOO^- + H_2O = RNH_2 + HCO_3^- \tag{2}$$

$$H_2O + CO_2 = H^+ + HCO_3^- \tag{3}$$

$$H_2O = H^+ + OH^- \tag{4}$$

$$HCO_3^- = H^+ + CO_3^{2-} \tag{5}$$

Equations 1 and 2 represent the amine protonation and the amine carbamate hydrolysis, respectively (*10*). Equations 3–5 are the typical ionization reactions for aqueous systems containing CO_2.

Since AMP has a tertiary carbon atom attached to the amino group, its carbamate ion is highly unstable and easily reverts to amine and bicarbonate (*3*). Chakraborty et al. (*11*) recently reported that carbamate ions could not be detected in CO_2 bearing AMP solutions, and they concluded that the bicarbonate and carbonate ions are the only major chemical sinks for CO_2.

The equilibrium constants representing the important reactions in the CO_2–AMP–H_2O system, in which water is present in excess, are given by

$$K_1 = [H^+][RNH_2]/[RNH_3^+] \tag{6}$$

$$K_3 = [H^+][HCO_3^-]/[CO_2] \tag{7}$$

$$K_4 = [H^+][OH^-] \tag{8}$$

$$K_5 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{9}$$

Although some values of K_1 (or pK_1 where $pK_1 = -(\log K_1)$) have been reported, they usually only apply to infinitely dilute solutions at 25 and 40 °C. Detailed information on pK_1 as a function of solution concentration and temperature is still lacking.

In addition to the above equilibrium equations, overall material and charge balances must also be satisfied:

$$[AMP] = [RNH_2] + [RNH_3^+] \tag{10}$$

$$\alpha[AMP] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{11}$$

$$[RNH_3^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \tag{12}$$

where [AMP] and α denote the total AMP concentration and the CO_2 loading of the AMP solution, respectively.

The physical solubility of CO_2 in the liquid phase is governed by Henry's law:

$$P_{CO_2} = H_{CO_2}[CO_2] \tag{13}$$

where P_{CO_2} and H_{CO_2} denote the partial pressure of carbon dioxide in the gas phase and Henry's law constant, respectively.

Equations 6–13 may be used to find the concentrations of seven species (i.e. $[RNH_2]$, $[H^+]$, $[RNH_3^+]$, $[HCO_3^-]$, $[CO_2]$, $[OH^-]$, $[CO_3^{2-}]$) and K_1 provided [AMP], α, P_{CO_2}, H_{CO_2}, K_3, K_4, and K_5 are given. The latter four parameters may be calculated from correlations derived by Kent and Eisenberg (*7*) since they were successful in representing CO_2 equilibria in aqueous solutions of conventional amines (*12*, *13*). These correlations, converted to SI units, may be summarized as follows (*13*):

$$K_3 = \exp(-241.818 + 298.253 \times 10^3 T^{-1} - 148.528 \times 10^6 T^{-2} + 332.648 \times 10^8 T^{-3} - 282.394 \times 10^{10} T^{-4}) \tag{14}$$

$$K_4 = \exp(39.5554 - 987.9 \times 10^2 T^{-1} + 568.828 \times 10^5 T^{-2} - 146.451 \times 10^8 T^{-3} + 136.146 \times 10^{10} T^{-4}) \tag{15}$$

$$K_5 = \exp(-294.74 + 364.385 \times 10^3 T^{-1} - 184.158 \times 10^6 T^{-2} + 415.793 \times 10^8 T^{-3} - 354.291 \times 10^{10} T^{-4}) \tag{16}$$

$$H_{CO_2} = \exp(22.2819 - 138.306 \times 10^2 T^{-1} + 691.346 \times 10^4 T^{-2} - 155.895 \times 10^7 T^{-3} + 120.037 \times 10^9 T^{-4})/7.50061 \tag{17}$$

A nonlinear equation solver called NDINVT, which is based on the generalized secant method and which is available from The University of British Columbia Computing Centre, was used to solve the equations numerically. Initial estimates of the concentrations and K_1 had to be provided. They were deduced, in part, from the approximate equilibrium reaction for the CO_2–AMP system suggested by Chakraboty et al. (*11*):

$$CO_2 + RNH_2 + H_2O = HCO_3^- + RNH_3^+ \tag{18}$$

The free amine concentration, $[RNH_2]$, is therefore approximately equal to $[AMP](1 - \alpha)$, and the concentrations of the reaction products, $[HCO_3^-]$ and $[RNH_3^+]$, equal approximately $\alpha[AMP]$. Since the pH of the solution usually falls into the range of 9–11 and the value of K_5 is normally in the order of 10^{-10} (kmol of ions)/m^3, the $[H^+]$ and $[CO_3^{2-}]$ were therefore small and equated to 10^{-10} and 10^{-8}, respectively. The following initial estimates were thus used:

$$[RNH_2] = [AMP](1.0 - \alpha) \qquad [H^+] = 10^{-10}$$

$$[RNH_3^+] = \alpha[AMP] \qquad [HCO_3^-] = \alpha[AMP]$$

$$[CO_2] = P_{CO_2}/H_{CO_2} \qquad [OH^-] = K_4/[H^+]$$

$$[CO_3^=] = 10^{-8} \qquad K_1 = 10^{-8}$$

Since the values of the unknown parameters range over several orders of magnitude, false convergence may occur. To be sure this does not happen, back calculations were performed by using a different nonlinear routine called QNEWT, which is based on a quasi-Newton method. By taking the K_1 values computed with NDINVT, P_{CO_2} or α values were recalculated and compared with the experimental results. The comparisons were always excellent and proved that false convergence had not arisen.

Results and Discussion

The CO_2 solubility data and the pK_1 values are summarized in Table I. To assess the validity of the results, the CO_2 solubilities in 2 and 3 M AMP solutions at 40.0 °C were compared with those reported previously (*3*, *5*). As shown in Fig-

Table I. Solubility of CO_2 in 2 M and 3 M AMP Solutions

		2 M AMP solution		3 M AMP solution	
temp, K	CO_2 partial pressure, kPa	CO_2 solubility[a]	pK_1	CO_2 solubility[a]	pK_1
293	98.93	0.960	9.343	0.898	9.161
293	49.88	0.900	9.316	0.846	9.272
293	19.28	0.880	9.704	0.830	9.680
293	8.39	0.815	9.842	0.763	9.854
293	3.23	0.781	10.242	0.747	10.342
313	94.00	0.940	9.339	0.875	9.170
313	47.05	0.841	9.167	0.815	9.267
313	18.01	0.768	9.373	0.714	9.399
313	7.94	0.704	9.576	0.643	9.589
313	2.70	0.620	9.864	0.582	9.949
333	82.66	0.830	8.994	0.809	9.116
333	41.14	0.735	9.015	0.683	9.056
333	16.46	0.600	9.066	0.546	9.107
333	8.00	0.476	9.059	0.427	9.104
333	1.90	0.375	9.410	0.321	9.405
353	53.33	0.618	8.720	0.524	8.658
353	25.84	0.463	8.638	0.394	8.621
353	10.40	0.291	8.507	0.247	8.514
353	4.99	0.212	8.504	0.169	8.458
353	1.59	0.154	8.692	0.126	8.673

[a] CO_2 solubility expressed in mol of CO_2/mol of AMP.

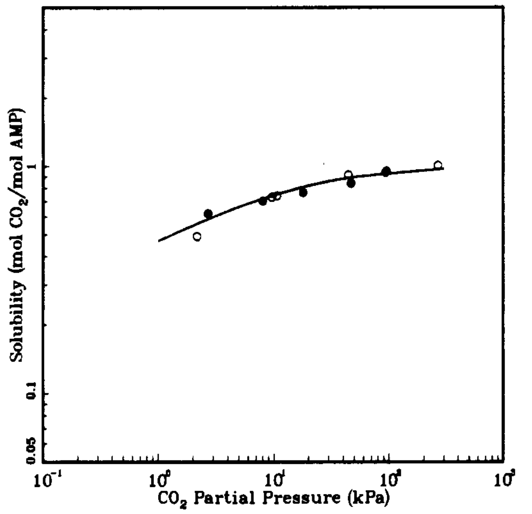

Figure 1. Solubility of CO_2 in a 2 M AMP solution at 40 °C: solid circles, present experimental data; open circles, Roberts and Mather (*5*); solid lines, present model.

ures 1 and 2, the agreement is very good, thereby validating the present experimental procedure.

The values of K_1 reported here are apparent equilibrium constants since system nonidealities were explicitly included in the model but lumped into K_1. The pK_1 values were found to be functions of temperature, $[CO_2]$, and [AMP]. Using $[CO_2]$ instead of α is preferable since the former can be calculated directly from P_{CO_2} and H_{CO_2}, as suggested by Chakma and Meisen (*13*). The correlation is

$$pK_1 = 2309.1 + 0.49828T - 70850(1/T) - 388.03(\ln T) - 6.3899[CO_2] - 0.095221(\ln [CO_2]) + 0.038508[AMP] \quad (19)$$

Table II provides a comparison between the pK_1 values found in this work and those reported earlier. The results predicted by eq 19 agree well with the data reported by Sartori and Savage (*3*) and Teng and Mather (*6*), but they are somewhat higher than those of Chakraborty et al. (*11*).

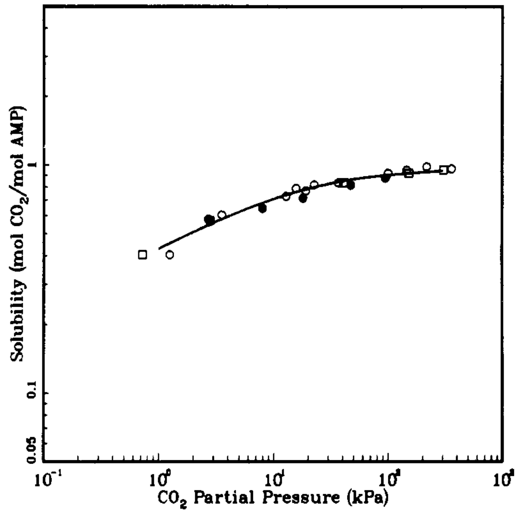

Figure 2. Solubility of CO_2 in a 3 M AMP solution at 40 °C: solid circles, present experimental data; open circles, Roberts and Mather (*5*); squares, Sartori and Savage (*3*); solid lines, present model.

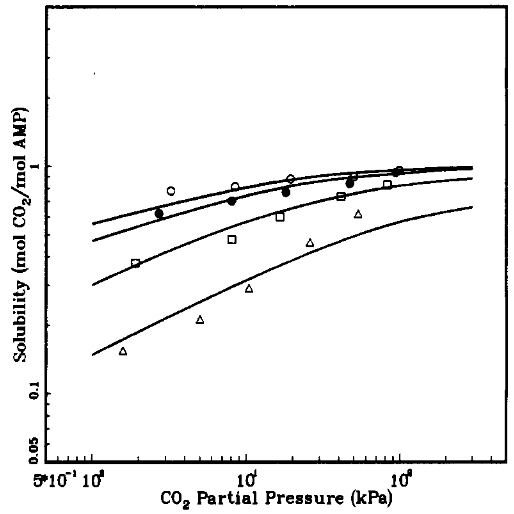

Figure 3. Solubility of CO_2 in a 2 M AMP solution at various temperatures: open circles, 20 °C; solid circles, 40 °C; squares, 60 °C; triangles, 80 °C; solid lines, present model.

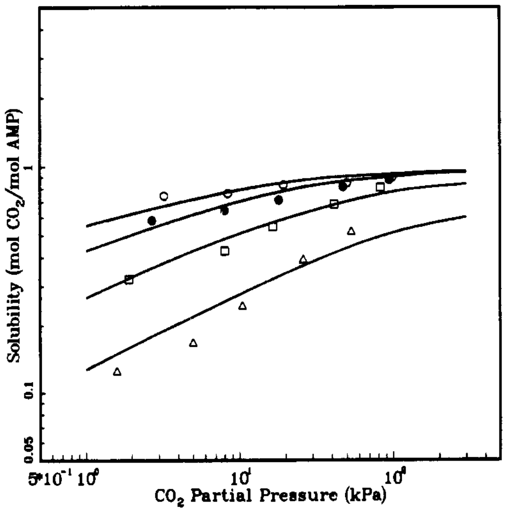

Figure 4. Solubility of CO_2 in a 3 M AMP solution at various temperatures: open circles, 20 °C; solid circles, 40 °C; squares, 60 °C; triangles, 80 °C; solid lines, present model.

When eq 19 is used to find K_1, then eqs 6–17 may be evaluated to obtain the concentrations of all species for a given set of operating conditions. As a result, the total CO_2 solubility, α, may be determined. The QNEWT routine was employed for this purpose, with the initial estimates of α falling into the range of 0.5–1.0 mol of CO_2/mol of AMP. As seen from Figures 1–4, good agreement was found between the predicted and mea-

Table II. Comparison of Present and Previously Reported pK_1 Values

source	temp, °C	AMP concn, M	CO_2 partial pressure, kPa	pK_1
Sartori and Savage (*3*)	40	3	0.7–305	9.70
Chakraborty et al. (*11*)	40	1–3	0–100	8.50
this work (eq 19)	40	3	10	9.67
Teng and Mather (*6*)	50	3.43	4–5650	9.11
this work (eq 19)	50	3.43	100	9.16

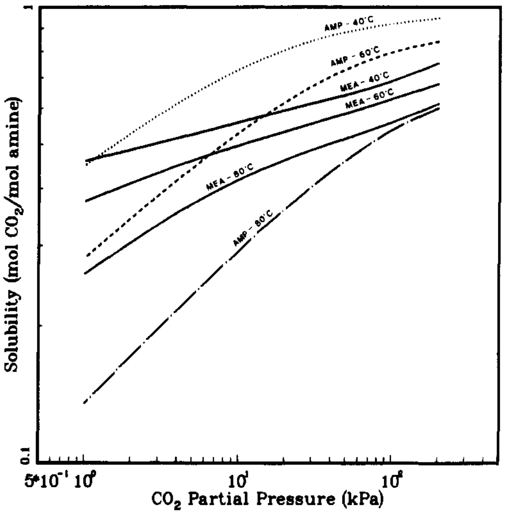

Figure 5. Solubility of CO_2 in 2.5 M AMP and MEA solutions at various temperatures: dotted, dashed, and chain-dotted lines, the present model predictions for the CO_2–AMP system at 40, 60, and 80 °C, respectively; solid lines, Kent–Eisenberg model (*7*) for the CO_2–MEA system at 40, 60, and 80 °C, respectively.

sured results; the mean square deviation was 6.0% for the runs shown in Table I. It should be noted that the solubility of CO_2 in AMP solution is a fairly weak function of temperature between 20 and 40 °C, but it becomes a significant function in the range of 60–80 °C.

The CO_2 solubilities in 2.5 M AMP and MEA solutions are shown in Figure 5. It is interesting to note that the CO_2 solubilities in AMP solutions are higher than those in MEA solutions at 40 °C. At 80 °C the opposite is true, and a crossover is seen at 60 °C. From the point of solubility, AMP solutions are therefore superior to MEA solutions for the regenerative separation of CO_2 since absorbers operate at low temperatures where α is large and desorbers operate at elevated temperatures where α is low. However, there are indications that the reaction and mass-transfer rates are lower for the CO_2–AMP system than for the CO_2–MEA system (*14*, *15*). Further research is therefore warranted on AMP reaction kinetics, mass-transfer rates, and stability.

Conclusions

The present experimental measurements significantly extend the previously reported results. The modified Kent–Eisenberg model represents the experimental data quite accurately and is well suited for use in the design of regenerative AMP separation processes.

Registry No. AMP, 124-68-5; CO_2, 124-38-9.

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