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Isothermal Vapor–Liquid Equilibrium of Binary Mixtures Containing Morpholine

Huey S. Wu, William E. Locke III, and Stanley I. Sandler*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

We report here measurements of the vapor–liquid equilibrium of morpholine, cyclooctane, and *n*-octane and of binary mixtures of morpholine separately with cyclooctane at 363.15 and 393.15 K, with *n*-octane at 353.35 and 383.35 K, with water at 348.35 and 368.35 K, and with 1-butanol at 363.35 and 383.35 K. These data are correlated with five liquid activity coefficient models using the maximum likelihood parameter estimation method, including a correction for nonideal vapor-phase behavior. The molar excess Gibbs free energy for mixtures containing morpholine + water is found to be positive in the morpholine-rich liquid region and negative in the water-rich region. The prediction of the UNIFAC model is poor for all the mixtures studied here, which confirms our hypothesis that the proximity effect is important for morpholine systems, and the cyclic secondary amine group in pyrrolidine and morpholine should be considered to be a different functional group from the noncyclic secondary amine group in group contribution methods.

Introduction

Cyclic amines and cyclic ethers are solvents of interest in the chemical industry and in theoretical modeling because of their unique physicochemical nature. We have previously reported vapor–liquid equilibrium (VLE) data for mixtures containing tetrahydrofuran (*1*), which has a single cyclic ether group, 1,3-dioxolane (*2*), which has two cyclic ether groups, and pyrrolidine (*3*), which has a single cyclic amine group. We measured the VLE of mixtures containing cyclic ethers in order to obtain activity coefficients in the liquid phase that are of use in determining the importance of homoproximity effects, that is, an interference effect between two neighboring identical nonalkyl functional groups on the same molecule, in current group contribution activity coefficient models (*4*). In this paper, we report the VLE data for mixtures containing morpholine. Morpholine has one cyclic ether group and one cyclic secondary amine group. We thought that the two nonalkyl functional groups in morpholine would also exhibit an electronic interference (now a heteroproximity effect) so that the contribution to thermodynamic properties of each of these groups would be different from those when there is no priximity effect (as in tetrahydrofuran or pyrrolidine). Another goal was to compare our measurements with the prediction of the UNIFAC model (*5*). In addition to determining the vapor pressure of pure morpholine, cyclooctane, and *n*-octane, four binary mixtures were measured, each at two isotherms: morpholine with cyclooctane at 363.15 and 393.15 K, with *n*-octane at 353.35 and 383.35 K, with water at 348.35 and 368.35 K, and with 1-butanol at 363.35 and 383.35 K.

Experiments

The experimental equipment and operating procedures have all been described in detail previously (*6*). The VLE measurements were done with a Stage–Muller dynamic still. The temperature was measured with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K. Pressures were measured with an accuracy of 0.02 kPa with use of a Wallace-Tiernan Model FA-187 precision mercury manometer. Vapor and liquid equilibrium samples were analyzed by using a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined in this way are accurate to better than 0.005 in mole fraction.

Table I. Vapor Pressures *P* of the Pure Components as a Function of Temperature *T*

morpholine		cyclooctane		*n*-octane	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
346.188	14.800	358.180	12.950	338.430	13.044
353.497	19.850	363.229	15.674	343.268	15.915
359.245	24.830	368.246	18.853	348.243	19.364
364.331	30.060	373.199	22.403	353.301	23.486
368.533	35.110	378.230	26.565	358.339	28.240
372.385	40.010	383.418	31.472	363.243	33.551
375.813	45.030	387.936	36.394	368.201	39.745
378.753	49.990	393.382	43.004	373.307	47.062
381.651	54.910	398.404	50.003	378.272	55.250
384.355	60.010	403.359	57.642	383.280	64.463
386.937	65.110	408.194	66.043	388.144	74.630
391.407	74.980	413.097	75.621	393.149	86.342
395.340	84.740				
399.106	94.630				
401.563	101.790				

Table II. Antoine Constants, Equation 1, for Pure Components and the Temperature Range of Determination

substance	A	B	C	temp range/K
1-butanol	6.379 87	1242.887	−106.574	350–387
water	7.075 10	1657.459	−46.130	333–373
morpholine	6.289 40	1447.651	−63.463	353–400
octane	6.044 07	1351.920	−64.034	348–390
cyclooctane	5.985 76	1437.722	−63.051	358–413

In this study, morpholine, cyclooctane, *n*-octane, and 1-butanol were of 99+% Gold Label quality from the Aldrich Chemical Co. Water was found as the main impurity in morpholine, cyclooctane, and 1-butanol. Thus, these chemicals were first purified to 99.9% by dehydration with molecular sieves. The water used was filtered, distilled, and deionized. The vapor pressures we measured for water and 1-butanol agree with literature values (*7*) to 0.1 kPa. The vapor pressures of morpholine, cyclooctane, and *n*-octane that we measured, listed in Table I, also agree with literature values (*7*–*9*). The vapor pressure data were fitted to the Antoine equation

$$\log (P/\text{kPa}) = A - \frac{B}{(T/\text{K}) + C} \tag{1}$$

The Antoine constants *A*, *B*, and *C* that we determined from our vapor pressure measurements are listed in Table II. The binary isothermal VLE data we measured are listed in Table III.

Results and Discussion

We correlated our measured vapor–liquid equilibrium data with the maximum likelihood parameter estimation method (*10*) using five liquid activity coefficient models that contain a nonideal gas-phase correction with virial coefficients from the

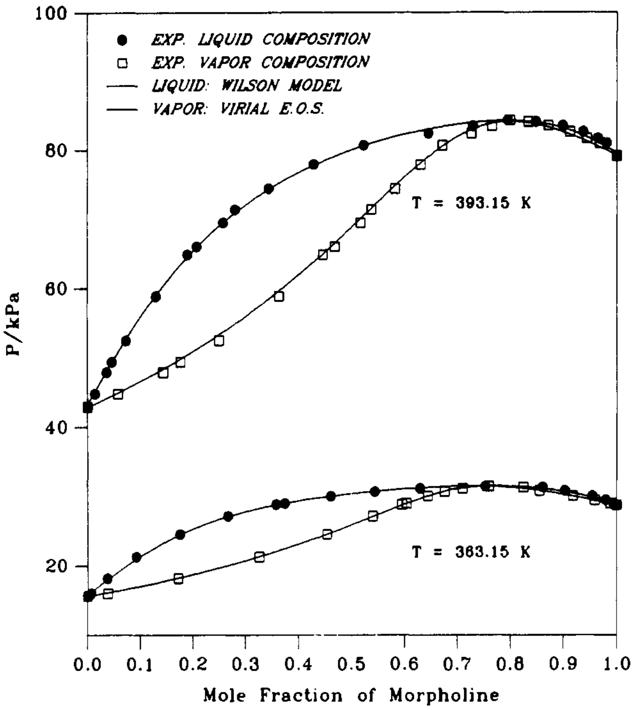

Figure 1. Vapor-liquid equilibrium (pressure vs mole fraction) for the morpholine (1) + cyclooctane (2) system at temperatures $T = 363.15$ and 393.15 K. The points are our experimental data, and the lines result from the Wilson model.

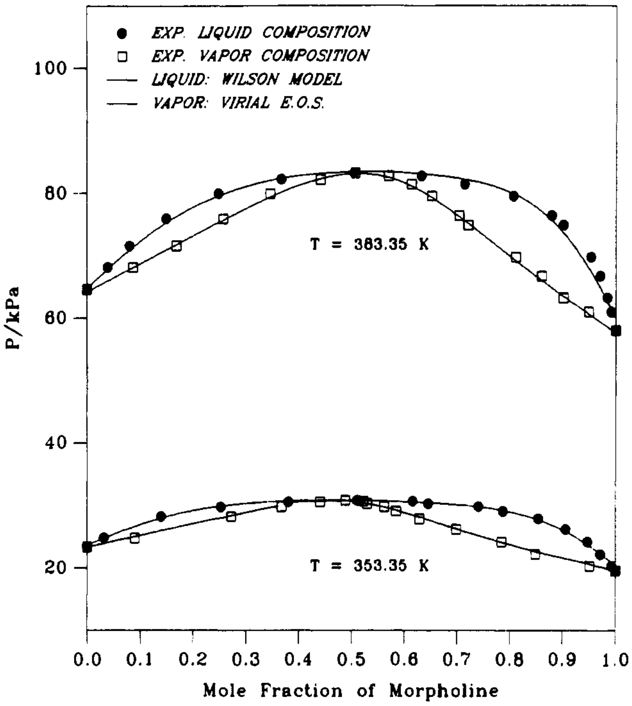

Figure 2. Vapor-liquid equilibrium (pressure vs mole fraction) for the morpholine (1) + *n*-octane (2) system at temperatures $T = 353.35$ and 383.35 K. The points are our experimental measurements, and the lines result from the Wilson model.

correlation of Hayden and O'Connell (*11*). The molar second virial coefficients and liquid molar volumes used here are listed in Table IV. The experimental data, together with the fit of the activity coefficient models that led to the best correlation, are plotted for each binary mixture in Figures 1-4. It is worth noting that some isobaric VLE data for morpholine + water have also been reported in the literature (*12-15*).

Among two-constant models, the Wilson model is best for correlating the experimental data for the morpholine + cyclooctane, morpholine + *n*-octane, and morpholine + 1-butanol mixtures, while the two-constant Margules model provides the best correlation of the morpholine + water mixture. It is interesting to compare the peculiar shape of the VLE phase envelope of the morpholine + water mixture in Figure 3 with that of the pyrrolidine + water mixture (*3*). Both are hydrogen-bonding mixtures in which there is a competition for hydrogen-bonding sites among the water + water, water +

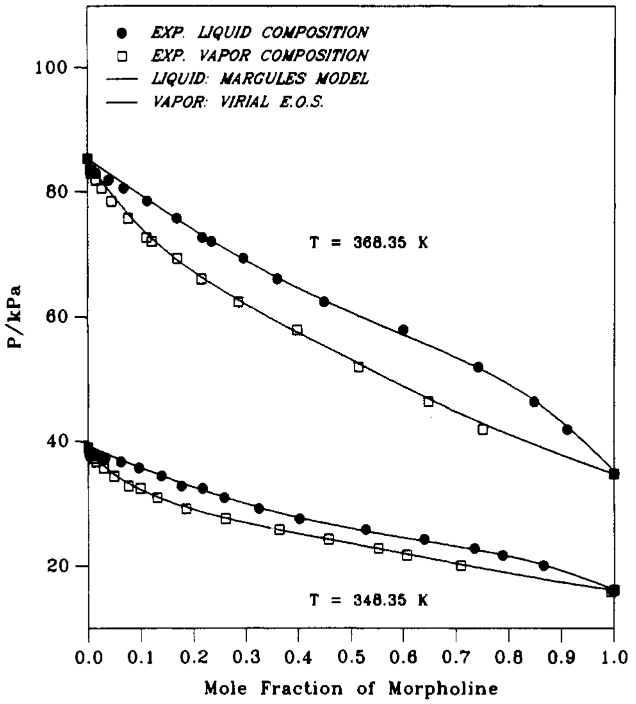

Figure 3. Vapor-liquid equilibrium (pressure vs mole fraction) for the morpholine (1) + water (2) system at temperatures $T = 348.35$ and 368.35 K. The points are our experimental measurements, and the lines result from the two-constant Margules model.

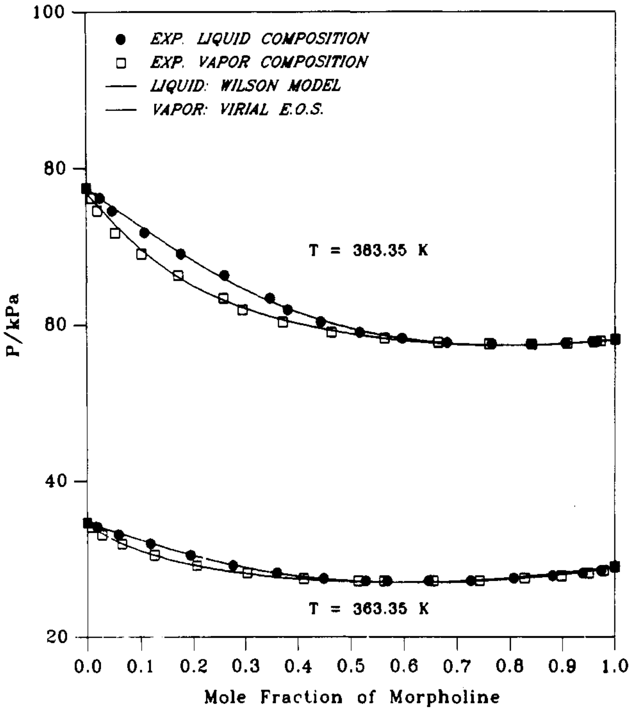

Figure 4. Vapor-liquid equilibrium (pressure vs mole fraction) for the morpholine (1) + 1-butanol (2) system at temperatures $T = 363.35$ and 383.35 K. The points are our experimental measurements, and the lines result from the Wilson model.

Table III. Experimental Vapor Pressure P, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1 of Binary Mixtures at Constant Temperature T

P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Morpholine (1) + n-Octane (2)						Morpholine (1) + Water (2)					
T = 353.35 K			T = 383.35 K			T = 348.35 K			T = 368.35 K		
23.330	0.0000	0.0000	64.586	0.0000	0.0000	38.978	0.0000	0.0000	85.354	0.0000	0.0000
24.800	0.0317	0.0900	68.100	0.0386	0.0865	38.140	0.0054	0.0021	83.500	0.0084	0.0044
28.240	0.1403	0.2723	71.540	0.0803	0.1696	37.810	0.0157	0.0046	82.990	0.0158	0.0061
29.790	0.2531	0.3674	75.880	0.1502	0.2582	37.310	0.0330	0.0096	81.880	0.0401	0.0153
30.610	0.3806	0.4404	79.910	0.2491	0.3471	36.700	0.0621	0.0151	80.570	0.0687	0.0269
30.850	0.5106	0.4880	82.260	0.3678	0.4408	35.710	0.0960	0.0299	78.480	0.1128	0.0451
30.730	0.6162	0.5226	83.330	0.5038	0.5070	34.390	0.1390	0.0494	75.740	0.1689	0.0771
30.320	0.6455	0.5294	82.830	0.6322	0.5699	32.820	0.1776	0.0771	72.640	0.2172	0.1116
29.840	0.7410	0.5617	81.510	0.7140	0.6135	32.440	0.2174	0.0997	72.020	0.2346	0.1215
29.100	0.7871	0.5841	79.620	0.8062	0.6521	30.920	0.2584	0.1311	69.320	0.2952	0.1696
27.910	0.8547	0.6282	76.480	0.8793	0.7044	29.170	0.3242	0.1862	66.020	0.3601	0.2152
26.200	0.9061	0.6982	74.950	0.9009	0.7213	27.570	0.4026	0.2606	62.320	0.4491	0.2858
24.180	0.9470	0.7843	69.830	0.9527	0.8110	25.850	0.5276	0.3634	57.850	0.5994	0.3983
22.200	0.9714	0.8488	66.800	0.9699	0.8600	24.280	0.6397	0.4567	51.900	0.7406	0.5132
20.320	0.9925	0.9508	63.290	0.9836	0.9017	22.820	0.7345	0.5518	46.300	0.8465	0.6466
19.590	1.0000	1.0000	61.030	0.9914	0.9489	21.710	0.7876	0.6065	41.900	0.9104	0.7500
			58.070	1.0000	1.0000	20.080	0.8651	0.7083	34.773	1.0000	1.0000
						15.870	0.9976	0.9944			
						16.140	1.0000	1.0000			
Morpholine (1) + Cyclooctane (2)						Morpholine (1) + 1-Butanol (2)					
T = 363.15 K			T = 393.15 K			T = 363.35 K			T = 383.35 K		
15.645	0.0000	0.0000	42.665	0.0000	0.0000	34.635	0.0000	0.0000	77.497	0.0000	0.0000
16.008	0.0065	0.0380	44.803	0.0140	0.0575	34.010	0.0190	0.0079	76.210	0.0256	0.0105
18.195	0.0372	0.1727	47.910	0.0360	0.1435	33.080	0.0584	0.0275	74.570	0.0483	0.0207
21.296	0.0924	0.3268	49.418	0.0459	0.1768	31.920	0.1187	0.0649	71.750	0.1090	0.0538
24.571	0.1764	0.4540	52.497	0.0727	0.2497	30.490	0.1943	0.1260	69.050	0.1776	0.1032
27.185	0.2676	0.5406	58.864	0.1300	0.3630	29.160	0.2760	0.2062	66.340	0.2604	0.1723
28.853	0.3588	0.5957	64.883	0.1899	0.4456	28.210	0.3598	0.3031	63.400	0.3472	0.2588
29.008	0.3752	0.6041	66.050	0.2076	0.4679	27.490	0.4483	0.4103	61.900	0.3807	0.2954
30.060	0.4610	0.6442	69.470	0.2577	0.5174	27.180	0.5277	0.5134	60.340	0.4426	0.3711
30.690	0.5448	0.6762	71.360	0.2799	0.5373	27.170	0.5679	0.5617	59.000	0.5166	0.4629
31.150	0.6295	0.7104	74.378	0.3438	0.5820	27.180	0.6457	0.6588	58.220	0.5968	0.5637
31.455	0.7533	0.7604	77.885	0.4286	0.6300	27.210	0.7249	0.7423	57.690	0.6819	0.6644
31.330	0.8616	0.8254	80.665	0.5228	0.6710	27.510	0.8068	0.8282	57.500	0.7657	0.7609
30.823	0.9031	0.8556	82.392	0.6444	0.7261	27.810	0.8811	0.8988	57.460	0.8390	0.8417
30.053	0.9549	0.9182	83.450	0.7288	0.7648	28.110	0.9381	0.9491	57.590	0.9054	0.9086
29.483	0.9796	0.9593	84.325	0.7946	0.7995	28.400	0.9780	0.9759	57.800	0.9559	0.9585
29.032	0.9941	0.9874	84.073	0.8482	0.8338	28.980	1.0000	1.0000	57.850	0.9654	0.9724
28.765	1.0000	1.0000	83.538	0.8986	0.8720				58.060	1.0000	1.0000
			82.610	0.9370	0.9121						
			81.695	0.9643	0.9435						
			81.000	0.9809	0.9678						
			79.144	1.0000	1.0000						

Table IV. Molar Second Virial Coefficients B_{ij} and Liquid Molar Volumes V_i as a Function of Temperature T

component	T/K	V_i/ ($\mathrm{cm^3\ mol^{-1}}$)	B_{ii}/ ($\mathrm{cm^3\ mol^{-1}}$)	B_{ij}/ ($\mathrm{cm^3\ mol^{-1}}$)
morpholine (i = 1)	348.35	92	−1348	
	353.35	93	−1296	
	363.15	94	−1205	
	363.35	94	−1203	
	368.35	94	−1161	
	383.35	96	−1048	
	393.15	97	−984	
cyclooctane (j = 2)	363.15	170	−2156	−1530
	393.15	176	−1716	−1231
n-octane (j = 2)	353.35	181	−2265	−1632
	383.35	189	−1800	−1306
water (j = 2)	348.35	19	−691	−472
	368.35	19	−502	−411
1-butanol (j = 2)	363.35	103	−1662	−1082
	383.35	106	−1210	−950

Table V. Calculated Azeotropic Mole Fraction x^{az} and Pressure P^{az} at Each Temperature T for the Systems Studied

mixtures	T/K	x_1^{az}	P^{az}/kPa
morpholine (1) + cyclooctane (2)	363.15	0.7588	31.524
	393.15	0.7929	84.209
morpholine (1) + n-octane (2)	353.35	0.4690	30.839
	383.35	0.5281	83.156
morpholine (1) + butanol (2)	363.35	0.6584	27.104
	383.35	0.7896	57.383

amine, and amine + amine pairs. The five molar excess Gibbs energy, G^E, models described earlier (*3*) are unable to give a satisfactory correlation for these strong nonideal hydrogen-bonding mixtures. It is interesting to note the unusual G^E of the morpholine + water mixture in Figure 5 in that it is negative in the water-rich region and positive in the morpholine-rich region. This suggests that the hydrogen bonding of morpholine + water is stronger than that of water + water, but weaker than that of morpholine + morpholine. Thus, although the shape of the morpholine + water phase envelope is unusual, the behavior is understandable. Also, the data for this system, and indeed for all the systems studied, satisfy the point-to-point thermodynamic consistency test. Finally, we note that if morpholine and water had closer vapor pressures, one would except to see a double azeotrope for this mixture based on the excess free energy behavior. All the azeotropes we did determine from the G^E models in this work are reported in Table V.

It is also interesting to compare the morpholine + 1-butanol mixture in Figure 5 with the pyrrolidine + ethanol mixture (*3*). Both are strongly solvating (amine + alcohol) mixtures in which the molar excess free energies are negative. It implies that although there is the possibility of hydrogen bonding among the alcohol + alcohol, alcohol + amine, and amine + amine groups, the alcohol + amine interaction is the strongest. This is the reason why the molar excess Gibbs free energies are negative in most alcohol + amine mixtures.

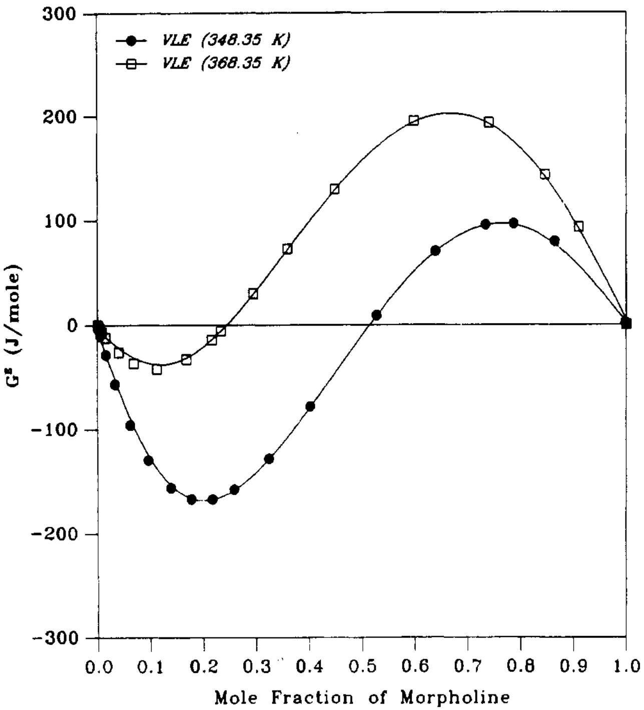

Figure 5. Molar excess Gibbs free energies, G^E, for the morpholine (1) + water (2) system. The points are generated from experimental VLE measurements, and the lines result from the three-constant Legendre polynomial expansion with $a_1 = -0.07429$, $a_2 = 0.47439$, and $a_3 = -0.12224$ at temperature $T = 348.35$ K and with $a_1 = 0.15580$, $a_2 = 0.32762$, and $a_3 = -0.10076$ 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

Paitoon Tontiwachwuthikul, Axel Meisen,* and Choon Jim Lim

Department of Chemical Engineering, The University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada

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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