Solubilities of Mixtures of Carbon Dioxide and Hydrogen Sulfide in Water + Diethanolamine + 2-Amino-2-methyl-1-propanol

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The solubilities of mixtures of carbon dioxide and hydrogen sulfide in water + diethanolamine (DEA) + 2-amino-2-methyl-1-propanol (AMP) have been measured at 40 °C and 80 °C and at partial pressures of acid gases ranging from 1.0 to 200 kPa. The ternary mixtures studied were 30 mass % AMP, 6 mass % DEA + 24 mass % AMP, 12 mass % DEA + 18 mass % AMP, 18 mass % DEA + 12 mass % AMP, 24 mass % DEA + 6 mass % AMP, and 30 mass % DEA aqueous solutions. The model of Deshmukh and Mather (1981) has been used to represent the solubility of mixtures of CO_2 and H_2S in the ternary solutions. The model reasonably reproduces the equilibrium partial pressures of CO_2 and H_2S above the ternary solutions for the systems tested.

Introduction

The removal of acidic gases such as CO_2, H_2S, and COS from gas streams is an important operation in the natural gas and synthetic ammonia industries, oil refineries, and petrochemical chemical plants. A wide variety of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), and *N*-methyldiethanolamine (MDEA) have been used industrially as gas-treating solvents (Kohl and Riesenfeld, 1985). Aqueous MEA solutions have been used almost exclusively due to their high reactivity, low solvent cost, low absorption of hydrocarbons, high alkalinity, and ease of reclamation from contaminated solutions (Isaacs et al., 1980). One disadvantage of MEA solutions is the fact that the MEA solutions are more corrosive than solutions of most other amines (Kohl and Riesenfeld, 1985). The MDEA is found to be an appropriate selective absorbent for H_2S in the presence of CO_2 (Goar, 1980; Yu and Astarita, 1987; Srinivasan and Aiken, 1988). Advantages of the use of MDEA solutions include their low vapor pressure, highly resistant to thermal and chemical degradation, high loading capacity (about 1.0 mol of CO_2/mol of amine), and low heat capacity and enthalpy of reaction with H_2S and CO_2 (Kohl and Riesenfeld, 1985; Riesenfeld and Brocoff, 1986). However, a slow reaction rate of CO_2 with tertiary amines limits the use of MDEA (Sartori and Savage, 1983).

Recently, the use of blended amines, a solution of two or more amines in varying compositions, has been shown to produce absorbents with excellent absorption characteristics as well as superior stripping qualities (Chakravarty et al., 1985). Blended amines combine the absorption characteristics of the constituent amines such as a higher loading capacity, faster reaction rates, and lesser energy requirement for regeneration. It has been shown that a primary or secondary amine, such as MEA or DEA, can be added to an aqueous MDEA solution to enhance the absorption rate of CO_2 without significantly affecting the energy requirements for stripping (Chakravarty et al., 1985; Austgen et al., 1991).

A different class of acid gas absorbents, the sterically hindered amines, have recently been disclosed as commercially attractive solvents for removal of acid gases from gaseous streams (Sartori and Savage, 1983; Say et al., 1984; Sartori et al., 1987). An example of the sterically hindered alkanolamines is 2-amino-2-methyl-1-propanol (AMP), which is the hindered form of MEA. Due to the bulkiness of the group attached to a tertiary carbon atom of AMP, an unstable carbamate would be formed when AMP reacts with CO_2, and this carbamate is readily hydrolyzed. Consequently, the reaction of CO_2 with AMP is mainly the formation of bicarbonate ion (Sartori and Savage, 1983; Yih and Shen, 1988). This would result in a theoretical ratio of 1.0 mol of CO_2/mol of amine. For CO_2 removal from gases by absorption in aqueous amine solutions and amine-promoted hot potassium carbonate, sterically hindered amines have been shown capacity and absorption rate advantages over conventional amines (Sartori and Savage, 1983). Compared to MDEA, AMP has the same CO_2 loading capacity (1.0 mol of CO_2/mol of amine) but has a higher reaction rate constant for the reaction with CO_2 (Li and Chang, 1994). H_2O + MEA + AMP has been suggested as a potential new solvent in addition to H_2O + MEA + MDEA for the acid gases treating process (Li and Chang, 1994).

Besides MEA, DEA aqueous solutions are also used extensively for the removal of CO_2 and H_2S from gas streams (Kohl and Riesenfeld, 1985). The low vapor pressure of DEA makes it suitable for low-pressure operations, as vaporization losses are quite negligible. In general, DEA solutions are less corrosive than MEA solutions because the acid gases are stripped easier and less vigorous reboiling is required. Due to the lower stability of the carbamate formed between CO_2 and DEA, as compared with that formed with MEA, higher CO_2 loadings of DEA may be obtained than those of MEA (Kohl and Riesenfeld, 1985). Thus, DEA may be considered to displace the MEA in the blended amine system H_2O + MEA + AMP, and the system H_2O + DEA + AMP results. The solubilities of CO_2 and H_2S in AMP and in DEA aqueous solutions have been reported in the literature for H_2O + AMP (Roberts and Mather, 1988; Teng and Mather, 1989, 1990; Tontiwachwuthikul et al., 1991) and for H_2O + DEA (Lee et al., 1972, 1973, 1974; Lawson and Garst, 1976). The equilibrium solubility of acid gases in H_2O + DEA + AMP has not yet been reported in the literature. It is the purpose of this research to measure the solubility of mixtures of CO_2 and H_2S in H_2O + DEA + AMP.

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Experimental Section

Alkanolamine aqueous solutions were prepared from distilled water. The distilled water was degassed by boiling. DEA is Riedel-de Haën reagent grade with a 99 mol % purity and AMP is Riedel-de Haën reagent grade with a 98 mol % purity. The gases were supplied from commercial cylinders with the following purities: CO_2, 99.9 mol %; H_2S, 99.5 mol %; N_2, 99.9 mol %. The materials, vapor−liquid equilibrium apparatus, and methods of analysis are the same as those used in our previous work (Li and Chang, 1994). The solubility of acidic gases in aqueous alkanolamine solutions was measured in a 1.0-L stainless steel vapor-recirculation equilibrium cell. The vapor−liquid equilibrium apparatus was mounted vertically in a thermostated oil bath. The temperature of the system was controlled by an immersion circulator to a stability within ±0.1 deg of the set-point temperature. The pressure of the system is indicated by an Ashcroft test gauge with the scale reading of 0.2 psi. To keep the total pressure of the system near 2 bar, nitrogen was normally introduced and mixed with acid gases, and the partial pressures of acid gases were determined by on-line chromatography. By varying the initial partial pressures of acid gases, the desired equilibrium partial pressures of acid gases can be obtained. It usually takes 6−8 h for the system to reach equilibrium. At equilibrium, a liquid sample was withdrawn from the equilibrium cell into a vessel containing excess 1.0 mol/L NaOH solution, thus converting free dissolved CO_2 into the nonvolatile ionic species. An excess amount of 0.5 mol/L $BaCl_2$ solution is then added to the solution. The solution is shaken well to permit all absorbed (physically and chemically) CO_2 to precipitate the carbonate as $BaCO_3$. The precipitate was put into an oven (60 °C) for 1 h and then is taken out and heated to 80 °C for 10 min to ripen the precipitate. The precipitate was then filtered out and washed with distiled water. The excess NaOH was titrated with HCl solution using phenolphthalein as the indicator. Using methyl orange as the indicator, a solution of HCl is then added. The amount of HCl added can be used to calculate the solubility of CO_2 in terms of the moles of CO_2 per mole of amine. The H_2S content of the sample was determined by reacting the liquid with a solution of acidified 1.0 mol/L I_2 (I^-). The unreacted I_2 was back-titrated with 0.1 mol/L $Na_2S_2O_3$ using starch as the indicator. The titration methods to determine loading capacity of the acid gases of solutions were similar to those of Teng and Mather (1989). The estimated experimental error in the measured solubility is about ±4−5%.

Table 1. Solubility of CO_2 in 2.0 kmol m^{-3} AMP Aqueous Solution at 40 °C and in 2.5 kmol m^{-3} MEA Aqueous Solution at 80 °C

P/kPa	α^a	P/kPa	α^a
	2.0 kmol m^{-3} AMP at 40 °C		
1.45	0.432	43.7	0.924
3.41	0.601	72.7	0.950
8.93	0.743	84.2	0.964
27.5	0.895	159.0	0.991
	2.5 kmol m^{-3} MEA at 80 °C		
3.57	0.363	61.4	0.550
8.62	0.420	70.9	0.564
20.0	0.479	121.8	0.580
24.5	0.481		

[a] Loading capacity = mol of acid gas/mol of amine.

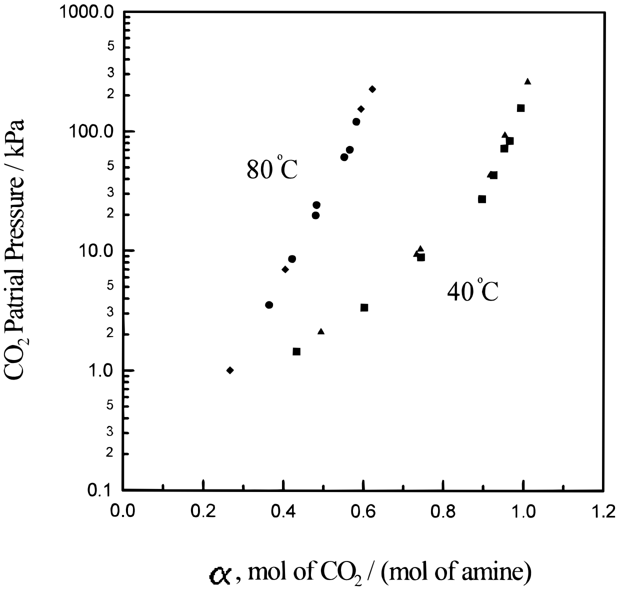

Figure 1. Solubility of CO_2 in 2.0 kmol m^{-3} AMP aqueous solution at 40 °C and in 2.5 kmol m^{-3} MEA aqueous solution at 80 °C. 2.0 kmol m^{-3} AMP at 40 °C: (■) this study; (▲) data of Roberts and Mather, 1988. 2.5 kmol m^{-3} MEA at 80 °C: (●) this study; (◆) data of Austgen et al., 1991.

Table 2. Solubility of H_2S in 2.0 kmol m^{-3} AMP Aqueous Solution at 40 °C and 2.5 kmol m^{-3} MEA Aqueous Solution at 80 °C

P/kPa	α^a	P/kPa	α^a
	2.0 kmol m^{-3} AMP at 40 °C		
2.69	0.618	13.1	0.834
2.93	0.630	30.3	0.904
5.46	0.726	68.8	0.970
8.82	0.794	178.0	1.021
9.79	0.793		
	2.5 kmol m^{-3} MEA at 80 °C		
2.18	0.172	75.0	0.705
18.9	0.477	115.2	0.792
42.6	0.614	147.8	0.833

[a] Loading capacity = mol of acid gas/mol of amine.

Results and Discussion

To test the vapor−liquid equilibrium apparatus and to confirm the sampling and analytical procedures, we have obtained data for systems of which data have been reported in the literature. Solubilities of CO_2 and H_2S in 2.0 kmol m^{-3} AMP aqueous solution at 40 °C and in 2.5 kmol m^{-3} MEA aqueous solution at 80 °C have been reported by Lee et al. (1976), Roberts and Mather (1988), and Austgen et al. (1991). The solubilities of CO_2 in 2.0 kmol m^{-3} AMP aqueous solution at 40 °C and in 2.5 kmol m^{-3} MEA aqueous solution at 80 °C measured in this study are presented in Table 1. The comparison of the measured results and the literature values (Roberts and Mather, 1988; Austgen et al., 1991) is shown in Figure 1. The CO_2 solubility measured in this study are within 5% of the literature values for 2.0 kmol m^{-3} AMP at 40 °C (Roberts and Mather, 1988) and within 4% of the literature values for 2.5 kmol m^{-3} MEA at 80 °C (Austgen et al., 1991) which is consistent with the estimated error of 4−5%. The solubilities of H_2S in 2.0 kmol m^{-3} AMP aqueous solution at 40 °C and in 2.5 kmol m^{-3} MEA aqueous solution at 80 °C have also been measured in this study. The results are presented in Table 2 and, along with the literature values (Lee et al., 1976; Roberts and Mather, 1988), are shown in Figure 2. The measured solubilities of H_2S are within 5% of the literature values for 2.0 kmol m^{-3} AMP at 40 °C (Roberts and Mather, 1988) and within 3% of the literature values for 2.5 kmol m^{-3} MEA at 80 °C (Lee et al., 1976). Except for the point of partial pressure of H_2S at 178 kPa,

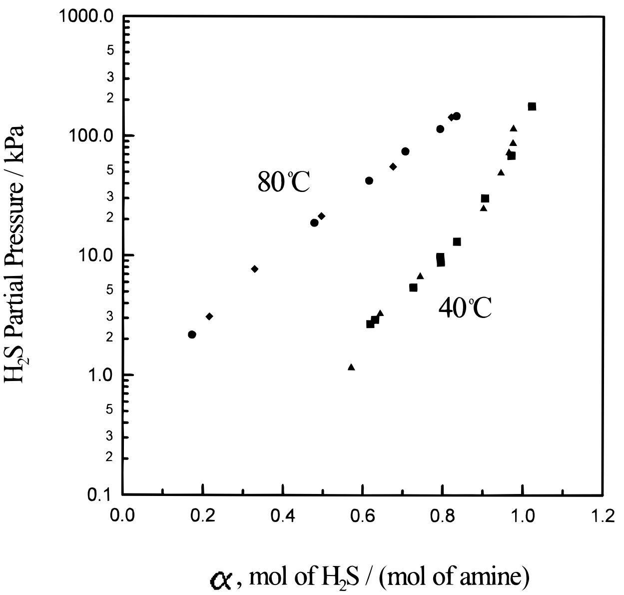

Figure 2. Solubility of H_2S in 2.0 kmol m^{-3} AMP aqueous solution at 40 °C and in 2.5 kmol m^{-3} MEA aqueous solution at 80 °C. 2.0 kmol m^{-3} AMP at 40 °C: (■) this study; (▲) data of Roberts and Mather, 1988. 2.5 kmol m^{-3} MEA at 80 °C: (●) this study; (◆) data of Lee et al., 1976.

Table 3. Solubility of Mixtures of CO_2 and H_2S in 3.43 mol/L AMP Aqueous Solution at 50 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
	This Study		
11.2	10.2	0.325	0.402
17.1	10.1	0.402	0.380
42.2	15.2	0.478	0.379
46.9	50.9	0.393	0.452
	Teng and Mather, 1989		
5.19	4.14	0.308	0.333
10.3	10.9	0.320	0.429
265.2	323.7	0.393	0.641
342.2	637.7	0.301	0.792
670.9	830.5	0.376	0.724

[a] Loading capacity = mol of acid gas/mol of amine.

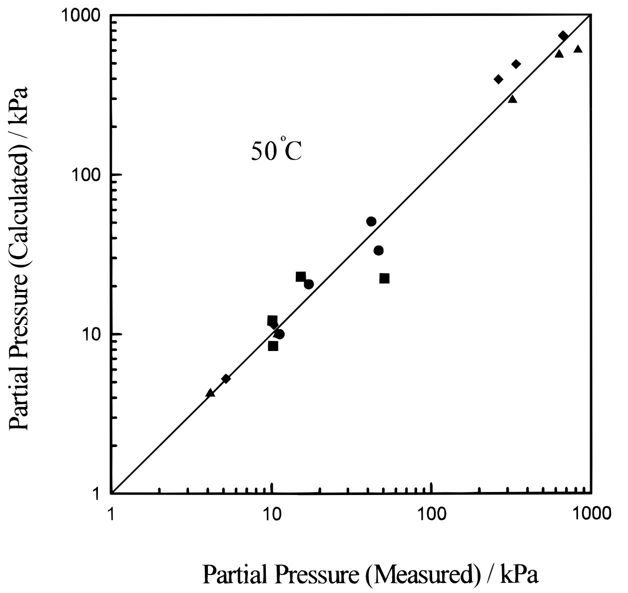

Figure 3. Comparison of predicted and measured partial pressures for CO_2 and H_2S in 3.43 kmol m^{-3} AMP aqueous solution at 50 °C: (●) CO_2, this study; (■) H_2S, this study; (◆) CO_2, data of Teng and Mather, 1989; (▲) H_2S, data of Teng and Mather, 1989. The predicated values are calculated by the model of Deshmukh and Mather.

Table 4. Solubility of Mixtures of CO_2 and H_2S in 30 mass % AMP Aqueous Solution at 40 °C and 80 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
	40 °C		
1.17	7.47	0.137	0.551
1.36	2.24	0.244	0.416
3.21	3.66	0.339	0.331
3.46	12.3	0.198	0.538
6.13	5.78	0.383	0.331
11.1	25.5	0.321	0.522
13.8	10.2	0.466	0.278
21.0	37.9	0.377	0.510
32.4	18.9	0.456	0.447
35.8	57.4	0.412	0.511
45.0	74.5	0.379	0.523
64.4	31.7	0.569	0.261
	80 °C		
4.58	2.89	0.170	0.231
5.22	2.69	0.174	0.234
6.44	3.69	0.193	0.213
7.59	3.47	0.205	0.213
8.77	3.85	0.236	0.172
9.84	4.00	0.239	0.194
10.5	34.8	0.110	0.493
12.2	4.47	0.287	0.173
16.2	4.50	0.293	0.187
17.9	5.32	0.306	0.177
22.7	5.30	0.330	0.178
24.0	5.79	0.328	0.178
24.5	44.0	0.164	0.479
34.1	6.83	0.382	0.156
52.5	8.48	0.431	0.146
74.2	10.1	0.490	0.146
75.9	12.6	0.468	0.179
83.8	14.7	0.492	0.167

[a] Loading capacity = mol of acid gas/mol of amine.

the solubility of H_2S in amine solutions measured in this study are in good agreement with the literature values, as shown in Figure 2. Besides the solubilities of CO_2 and H_2S in AMP aqueous solution, the solubilities of mixtures of CO_2 and H_2S in 3.43 kmol m^{-3} AMP aqueous solution at 50 °C are also determined in this study. Along with the literature values (Teng and Mather, 1989) the solubilities of mixtures of CO_2 and H_2S in 3.43 kmol m^{-3} AMP aqueous solution are presented in Table 3. In Figure 3, the comparison between experimental data, the literature values (Teng and Mather, 1989), and the calculated values by the model Deshmukh and Mather (to be described shortly) are shown. The calculated values for solubilities of mixtures of CO_2 and H_2S in AMP solution by the model Deshmukh and Mather are generally in good agreement with both the measured values obtained in this work and the literature values (Teng and Mather, 1989).

For the measurements of solubility of mixtures of CO_2 and H_2S in H_2O + DEA + AMP, the systems studied were 30 mass % AMP, 6 mass % DEA + 24 mass % AMP, 12 mass % DEA + 18 mass % AMP, 18 mass % DEA + 12 mass % AMP, 24 mass % DEA + 6 mass % AMP, and 30 mass % DEA aqueous solutions. The temperatures studied are 40 and 80 °C. The measured solubilities of mixtures of CO_2 and H_2S over H_2O + DEA + AMP are presented in Tables 4−9. The partial pressures of acid gases range from 0.1 to 140 kPa and 0.4 to 120 kPa, for CO_2 and H_2S, respectively. The partial pressures of acid gases are specified by changing the initial values of the partial pressures of acid gases to cover the desired partial pressure range of the acid gases. When two acid gases coexist in a

Table 5. Solubility of Mixtures of CO_2 and H_2S in 6 mass % DEA + 24 mass % AMP Aqueous Solution at 40 °C and 80 °C

P/kPa		α^a	
CO_2	H_2S	CO_2	H_2S
	40 °C		
0.11	0.69	0.088	0.334
0.27	0.64	0.198	0.334
0.46	1.35	0.233	0.416
0.60	2.25	0.212	0.375
0.79	6.28	0.153	0.532
1.44	3.46	0.273	0.397
2.09	2.66	0.371	0.390
2.30	12.1	0.226	0.521
4.70	15.5	0.296	0.484
10.1	11.0	0.348	0.384
10.2	24.5	0.328	0.484
12.1	8.39	0.472	0.312
32.8	49.3	0.354	0.484
38.6	18.4	0.559	0.351
51.3	36.7	0.500	0.318
61.0	25.6	0.612	0.310
64.8	49.1	0.480	0.338
	80 °C		
1.06	1.53	0.087	0.199
1.92	1.56	0.112	0.167
3.71	2.27	0.149	0.209
6.60	3.00	0.220	0.204
11.3	3.75	0.261	0.195
12.2	12.4	0.250	0.280
15.5	19.6	0.238	0.302
18.2	5.10	0.310	0.198
26.4	29.3	0.239	0.341
43.3	8.65	0.407	0.205
64.0	9.67	0.464	0.193
94.0	86.3	0.336	0.430
95.0	17.1	0.540	0.176

[a] Loading capacity = mol of acid gas/mol of amine.

system, the solubility of one of the acid gases will normally be affected and competed with by the other acid gas.

For the purpose of design calculations, it is difficult to use the solubility data directly from the measurements. A correlation to represent the solubility of acidic gases in alkanolamine solutions is normally required for practical applications. In this study, the method proposed by Deshmukh and Mather (1981) will be applied to correlate the measured solubility data of mixtures of CO_2 and H_2S in H_2O + DEA + AMP solutions.

The main reactions occurring in the $CO_2 + H_2S + H_2O$ + DEA + AMP system are as follows:

$$R_2NH_2^+ \leftrightarrow H^+ + R_2NH \quad (1)$$

$$R'NH_3^+ \leftrightarrow H^+ + R'NH_2 \quad (2)$$

$$R_2NCOO^- + H_2O \leftrightarrow R_2NH + HCO_3^- \quad (3)$$

$$H_2O + CO_2 \leftrightarrow H^+ + HCO_3^- \quad (4)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (5)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (6)$$

$$H_2S \leftrightarrow H^+ + HS^- \quad (7)$$

$$HS^- \leftrightarrow H^+ + S^{2-} \quad (8)$$

Table 6. Solubility of Mixtures of CO_2 and H_2S in 12 mass % DEA + 18 mass % AMP Aqueous Solution at 40 °C and 80 °C

P/kPa		α^a	
CO_2	H_2S	CO_2	H_2S
	40 °C		
0.11	0.34	0.191	0.296
0.21	0.60	0.195	0.279
1.18	2.30	0.296	0.320
1.49	1.48	0.381	0.287
2.60	16.6	0.186	0.497
3.79	5.02	0.375	0.316
6.94	3.71	0.462	0.221
15.7	12.3	0.482	0.301
19.0	41.9	0.279	0.475
29.7	9.12	0.559	0.238
70.4	14.8	0.659	0.149
72.3	30.5	0.587	0.284
83.1	59.0	0.461	0.377
87.5	67.9	0.468	0.368
91.2	16.0	0.661	0.117
	80 °C		
1.60	3.73	0.110	0.217
2.88	1.63	0.158	0.123
3.91	4.63	0.193	0.197
5.36	15.6	0.128	0.323
6.90	10.1	0.188	0.270
7.20	5.46	0.223	0.205
12.4	6.94	0.282	0.190
13.6	12.3	0.266	0.259
13.7	20.6	0.191	0.291
15.0	29.1	0.170	0.369
22.8	15.2	0.315	0.280
23.7	26.0	0.227	0.272
33.9	18.1	0.354	0.241
97.1	41.7	0.409	0.283
101.4	45.5	0.429	0.262

[a] Loading capacity = mol of acid gas/mol of amine.

where R_2NH and $R'NH_2$ denote DEA and AMP, respectively. The following balance equations for the reacting species can be formed:

Electroneutrality:

$$[R_2NH_2^+] + [R'NH_3^+] + [H^+] = [R_2NCOO^-] + [HCO_3^-] + [OH^-] + 2[CO_3^{2-}] + [HS^-] + 2[S^{2-}] \quad (9)$$

Mass balances:

$$[R_2NH] + [R_2NCOO^-] + [R_2NH_2^+] = m_1 \quad (10)$$

$$[R'NH_2] + [R'NH_3^+] = m_2 \quad (11)$$

$$[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [R_2NCOO^-] = (m_1 + m_2)\alpha_{CO_2} \quad (12)$$

$$[H_2S] + [HS^-] + [S^{2-}] = (m_1 + m_2)\alpha_{H_2S} \quad (13)$$

where m_1 and m_2 are the molality of DEA and AMP, respectively, and α_{CO_2} and α_{H_2S} are the loading capacity of CO_2 and H_2S, respectively.

The following thermodynamic equilibrium constant expressions can be written:

$$K_{11} = \gamma(R_2NH)\gamma(H^+)m(R_2NH)m(H^+)/\gamma(R_2NH_2^+)m(R_2NH_2^+) \quad (14)$$

$$K_{12} = \gamma(R'NH_2)\gamma(H^+)m(R'NH_2)m(H^+)/\gamma(R'NH_3^+)m(R'NH_3^+) \quad (15)$$

Table 7. Solubility of Mixtures of CO_2 and H_2S in 18 mass % DEA + 12 mass % AMP Aqueous Solution at 40 °C and 80 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
	40 °C		
0.13	0.72	0.157	0.140
0.39	1.46	0.233	0.207
0.61	1.43	0.252	0.163
1.58	2.57	0.343	0.258
3.28	33.0	0.131	0.588
4.70	4.61	0.426	0.269
12.8	8.08	0.467	0.275
13.5	56.0	0.207	0.540
32.3	13.5	0.516	0.273
52.5	17.5	0.554	0.236
65.2	24.8	0.616	0.177
73.0	23.9	0.605	0.220
88.1	22.9	0.616	0.207
	80 °C		
1.20	3.33	0.131	0.230
2.95	4.33	0.148	0.235
3.78	4.77	0.192	0.200
4.32	7.35	0.169	0.197
4.98	7.71	0.173	0.258
5.82	5.46	0.223	0.222
8.77	9.64	0.229	0.244
12.6	8.47	0.261	0.218
14.9	11.5	0.277	0.234
16.8	8.21	0.303	0.226
24.4	14.3	0.334	0.224
30.0	12.4	0.364	0.226
39.9	17.9	0.381	0.248
46.5	59.7	0.254	0.369
50.2	67.0	0.236	0.468
70.0	15.7	0.441	0.200
123.2	56.4	0.408	0.279

[a] Loading capacity = mol of acid gas/mol of amine.

Table 8. Solubility of Mixtures of CO_2 and H_2S in 24 mass % DEA + 6 mass % AMP Aqueous Solution at 40 °C and 80 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
	40 °C		
0.21	0.82	0.121	0.195
0.33	1.53	0.212	0.175
0.64	1.98	0.195	0.311
2.72	8.32	0.301	0.302
3.61	9.15	0.306	0.320
3.95	40.0	0.153	0.576
6.36	14.2	0.366	0.341
13.1	63.5	0.216	0.502
27.1	30.2	0.427	0.282
35.6	34.5	0.472	0.271
46.5	56.6	0.410	0.331
50.0	36.7	0.520	0.253
51.9	43.0	0.503	0.290
56.2	40.2	0.522	0.270
68.9	42.6	0.531	0.235
103.4	71.1	0.535	0.308
108.9	85.3	0.507	0.337
	80 °C		
1.07	4.52	0.081	0.210
1.41	2.59	0.109	0.207
5.36	7.87	0.178	0.234
7.06	2.85	0.252	0.161
7.59	8.04	0.232	0.289
15.3	3.58	0.340	0.163
16.6	11.9	0.286	0.291
26.8	14.0	0.368	0.282
27.5	5.52	0.393	0.166
41.4	16.8	0.361	0.306
41.9	6.66	0.422	0.161
57.3	95.1	0.255	0.481
59.9	19.8	0.421	0.300
75.1	21.7	0.436	0.318
80.3	8.84	0.504	0.156
139.1	49.0	0.483	0.323

[a] Loading capacity = mol of acid gas/mol of amine.

$$K_{21} = \gamma(\mathrm{R_2NH})\gamma(\mathrm{HCO_3}^-)m(\mathrm{R_2NH})m(\mathrm{HCO_3}^-)/\gamma(\mathrm{R_2NCOO}^-)m(\mathrm{R_2NCOO}^-)a_{\mathrm{W}} \quad (16)$$

$$K_3 = \gamma(\mathrm{H}^+)\gamma(\mathrm{HCO_3}^-)m(\mathrm{H}^+)m(\mathrm{HCO_3}^-)/\gamma(\mathrm{CO_2})m(\mathrm{CO_2})a_{\mathrm{W}} \quad (17)$$

$$K_4 = \gamma(\mathrm{H}^+)\gamma(\mathrm{OH}^-)m(\mathrm{H}^+)m(\mathrm{OH}^-)/a_{\mathrm{W}} \quad (18)$$

$$K_5 = \gamma(\mathrm{H}^+)\gamma(\mathrm{CO_3}^{2-})m(\mathrm{H}^+)m(\mathrm{CO_3}^{2-})/\gamma(\mathrm{HCO_3}^-)m(\mathrm{HCO_3}^-) \quad (19)$$

$$K_6 = \gamma(\mathrm{H}^+)\gamma(\mathrm{HS}^-)m(\mathrm{H}^+)m(\mathrm{HS}^-)/\gamma(\mathrm{H_2S})m(\mathrm{H_2S}) \quad (20)$$

$$K_7 = \gamma(\mathrm{H}^+)\gamma(\mathrm{S}^{2-})m(\mathrm{H}^+)m(\mathrm{S}^{2-})/\gamma(\mathrm{HS}^-)m(\mathrm{HS}^-) \quad (21)$$

As in the work of Deshmukh and Mather (1981), the activity of the water, a_{W}, has been set equal to its mole fraction. The extended Debye−Hückel expression given by Guggenheim (1935) has been used to obtain the activity coefficient of species

$$\ln \gamma_i = -\frac{A z_i^2 I^{0.5}}{1 + I^{0.5}} + 2\sum_j \beta_{ij} m_j \quad (22)$$

The first term accounts for the electrostatic effects of the solvent on the solute species at infinite dilution. The second term takes into account short-range van der Waals forces. The β_{ij} is the specific interaction coefficient for the *ij* pair, and *I* is the ionic strength of the solution

$$I = \frac{1}{2}\sum m_i z_i^2 \quad (23)$$

where z_i is the ion charge on species *i*. The coefficient *A* in eq 22, the Debye−Hückel proportionality factor, is a function of the dielectric constant and density of the solvent and has the following expression (Pitzer, 1973):

$$A = \left(\frac{2\pi N_0 d_{\mathrm{w}}}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \quad (24)$$

where N_0 is the Avogadro constant, d_{w} is the density of solvent, *e* is the elementary charge, *D* is the dielectric constant, and *k* is the Boltzmann constant. The density of water was obtained, in this study, from the equation of state of Keenan et al. (1969). The dielectric constant of water is calculated by the equation proposed by Bradley and Pitzer (1979).

The vapor−liquid equilibrium for the acid gas species is given by

$$\phi_{\mathrm{CO_2}} y_{\mathrm{CO_2}} P = \gamma_{\mathrm{CO_2}} m_{\mathrm{CO_2}} \mathrm{H}_{\mathrm{CO_2}} \quad (25)$$

$$\phi_{\mathrm{H_2S}} y_{\mathrm{H_2S}} P = \gamma_{\mathrm{H_2S}} m_{\mathrm{H_2S}} H_{\mathrm{H_2S}} \quad (26)$$

The fugacity coefficients were calculated using the Peng−Robinson equation of state (Peng and Robinson, 1976). Since the total pressure of the system is not normally reported in the literature, the fugacity coefficient of an acid gas in the gaseous mixture was approximated

Table 9. Solubility of Mixtures of CO_2 and H_2S in 30 mass % DEA Aqueous Solution at 40 °C and 80 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
	40 °C		
0.36	4.83	0.159	0.312
0.56	4.12	0.159	0.406
1.09	4.44	0.229	0.204
1.70	23.5	0.193	0.509
2.18	7.84	0.230	0.379
3.12	11.3	0.331	0.350
7.23	40.7	0.254	0.508
13.9	13.5	0.435	0.181
18.8	58.7	0.307	0.465
29.6	111.3	0.347	0.439
44.5	30.4	0.413	0.438
47.5	33.2	0.475	0.355
85.3	99.7	0.410	0.363
92.2	123.3	0.396	0.418
100.7	69.3	0.531	0.328
	80 °C		
0.99	4.89	0.096	0.229
1.62	6.70	0.106	0.182
1.81	5.41	0.103	0.263
2.25	6.06	0.138	0.248
2.66	8.75	0.119	0.286
3.49	6.74	0.177	0.237
4.47	42.0	0.100	0.405
5.19	8.65	0.182	0.220
5.89	11.5	0.149	0.306
7.45	8.92	0.222	0.252
10.9	25.9	0.192	0.329
12.6	10.7	0.253	0.228
16.0	34.5	0.206	0.358
16.9	11.4	0.285	0.196
22.9	13.4	0.301	0.215
30.2	13.9	0.337	0.190
44.8	14.6	0.360	0.199
47.9	17.1	0.363	0.249
95.2	32.1	0.428	0.250

[a] Loading capacity = mol of acid gas/mol of amine.

Table 10. Effect of Temperature on Equilibrium Constants and Henry's Constants

equilibrium constant	a_1	a_2	a_3	a_4
K_{11}[a]	−10.3500	−0.371554		
K_{21}[a]	−3.4749	−0.625331		
K_{12}[a]	10.1115	−0.336779		
K_3[b]	235.482	−12092.1	−36.7816	
K_4[b]	140.932	−13445.9	−22.4773	
K_5[b]	220.067	−12431.7	−35.4819	
K_6[b]	218.599	−12995.4	−33.5471	
K_7[b]	136.915	−13445.9	−22.4773	
H_{CO_2}[c]	94.4914	−6789.04	−11.4519	−0.010454
H_{H_2S}[c]	342.595	−13236.8	−55.0551	0.0595651

[a] Determined in this study, K_{11} and K_{21} for DEA; K_{12} for AMP. [b] $\ln K_i = a_1 + a_2/(T/\mathrm{K}) + a_3 \ln(T/\mathrm{K})$ where a_i are values reported by Edwards et al., 1978. [c] $\ln H_i/(\mathrm{kg\ atm})/\mathrm{mol} = a_1 + a_2/(T/\mathrm{K}) + a_3 \ln(T/\mathrm{K}) + a_4(T/\mathrm{K})$ where a_i are values reported by Edwards et al., 1978.

Table 11. Specific Interaction Parameters for $CO_2 + H_2S + H_2O +$ DEA + AMP

binary pair[a]	kg/mol
$\beta(R_2NH - R_2NH_2^+)$	0.035469
$\beta(R_2NH - R_2NCOO^-)$	−0.252955
$\beta(R_2NH - HCO_3^-)$	0.387285
$\beta(R_2NH_2^+ - R_2NCOO^-)$	0.020740
$\beta(R_2NH_2^+ - HCO_3^-)$	−0.013300
$\beta(R'NH_2 - R'NH_3^+)$	−0.024549
$\beta(R'NH_2 - HCO_3^-)$	−0.096729
$\beta(R'NH_3^+ - HCO_3^-)$	0.024209
$\beta(R_2NH - R'NH_3^+)$	0.045440
$\beta(R_2NH_2^+ - R'NH_2)$	0.535108
$\beta(R_2NCOO^- - R'NH_2)$	0.061389
$\beta(R_2NCOO^- - R'NH_3^+)$	0.009326
$\beta(R_2NH_2^+ - CO_2)$	−0.195899
$\beta(R_2NCOO^- - CO_2)$	0.494019
$\beta(R'NH_3^+ - CO_2)$	4.558870
$\beta(R_2NH - HS^-)$	−0.007853
$\beta(R_2NH_2^+ - H_2S)$	−0.060475
$\beta(R_2NH_2^+ - HS^-)$	0.028441
$\beta(R_2NCOO^- - H_2S)$	−0.601068
$\beta(R'NH_2 - HS^-)$	−0.042278
$\beta(R'NH_3^+ - H_2S)$	−0.050163
$\beta(R'NH_3^+ - HS^-)$	−0.019718

[a] R_2NH and $R'NH_2$ denote DEA and AMP, respectively.

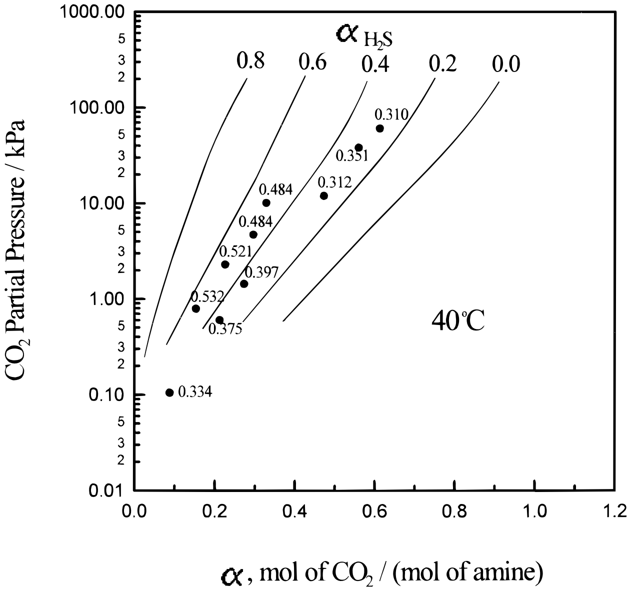

Figure 4. Effects of the presence of H_2S on the partial pressures of CO_2 over 6 mass % DEA + 24 mass % AMP aqueous solution at 40 °C. The specified value denotes H_2S loading of the solution. The lines show the values calculated by the model of Deshmukh and Mather. The points show the data points.

by the value of the fugacity coefficient of the acid gas (pure gas) at its partial pressure. For the low pressure of the system, this approximation may only introduce negligible errors. In the calculation, the effect of interaction among gases is lumped into the parameters introduced in the liquid phase.

In this study, the equilibrium constants for K_3 to K_7 and Henry's constants for CO_2 and H_2S were adopted directly from the literature values (Edwards et al., 1978) and are listed in Table 10. Using the least-squares fit to the measured solubility data of mixtures of CO_2 and H_2S in H_2O + DEA + AMP, i.e., solubility data in Tables 4−9, the equilibrium constants for K_{11}, K_{21}, and K_{12}, and the specific interaction parameters β_{ij} were determined. The determined equilibrium constants are also presented in Table 10, and the specific interaction parameters β_{ij} are presented in Table 11. The average absolute percentage deviation is about 31% for both CO_2 and H_2S. This deviation reflects the greater inaccuracy involved in experiments with two acid gases as well as the inadequacy of the model. As mentioned in Figure 3, the calculated values are based on the model of Deshmukh and Mather. In Figure 4, the comparison between the calculated and experimental CO_2 partial pressure over 6 mass % DEA + 24 mass % AMP aqueous solution at various H_2S loading capacities at 40 °C is shown. The solid lines of equal H_2S loading were generated the model of Deshmukh and Mather. The solubility of CO_2 over H_2O + DEA + AMP is affected by the H_2S loading capacity of the solution; the

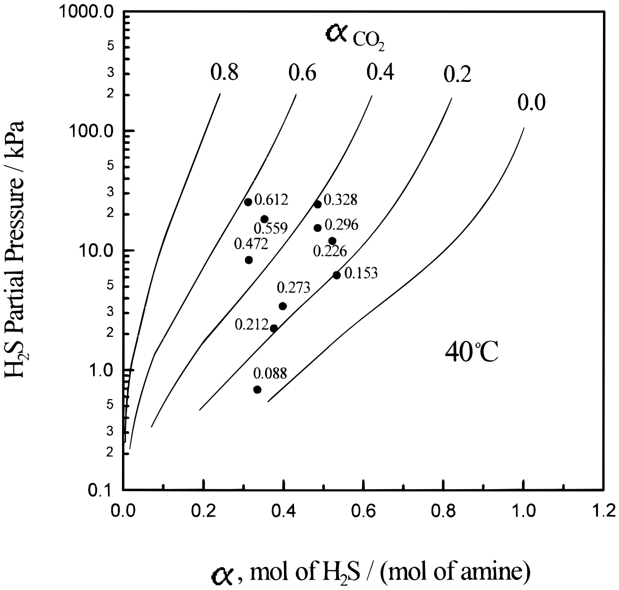

Figure 5. Effect of the presence of CO_2 on the partial pressures of H_2S over 6 mass % DEA + 24 mass % AMP aqueous solution at 40 °C. The specified value denotes CO_2 loading of the solution. The lines show the values calculated by the model of Deshmukh and Mather. The points show the data points.

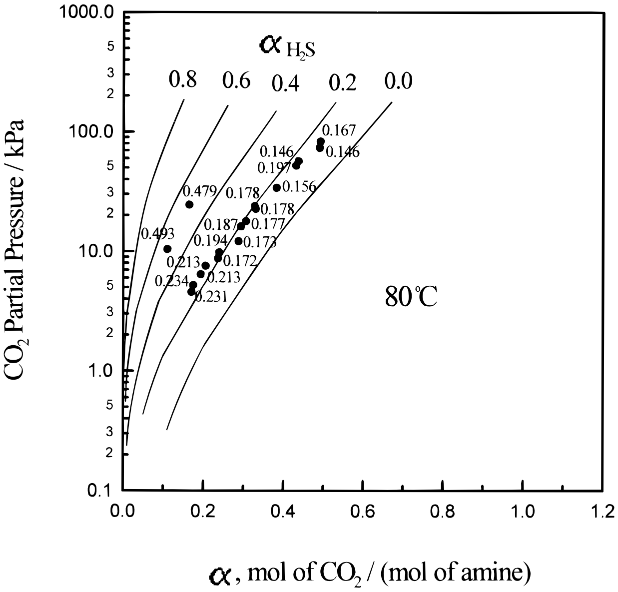

Figure 6. Effect of the presence of H_2S on the partial pressures of CO_2 over 30 mass % AMP aqueous solution at 80 °C. The specified value denotes H_2S loading of the solution. The lines show the values calculated by the model of Deshmukh and Mather. The points show the data points.

higher the H_2S loading capacity of the solution observed, the lower the CO_2 loading capacity of the solution obtained, as shown in Figure 4. A plot of partial pressures of H_2S over 6 mass % DEA + 24 mass % AMP aqueous solution at various CO_2 loading capacities at 40 °C is shown in Figure 5. The loading of H_2S of the solution is influenced by the CO_2 loading of the solution. At a particular partial pressure of H_2S, the lower CO_2 loading capacity of the solution is observed, and the higher H_2S loading capacity of the solution is also presented, as shown in Figure 5. The calculated solubilities of acid gases over H_2O + DEA + AMP by the model of Deshmukh and Mather are generally in good agreement with experimental data, as shown in Figures 4 and 5. In Figure 6, the comparison between the calculated and experimental solubility of CO_2 over 30 mass % AMP aqueous solution at various H_2S loading capacities at 80 °C is shown. As shown in Figure 6, the calculated solubility of CO_2 over H_2O + DEA + AMP by the model of Deshmukh and Mather are generally in good agreement with experimental data.

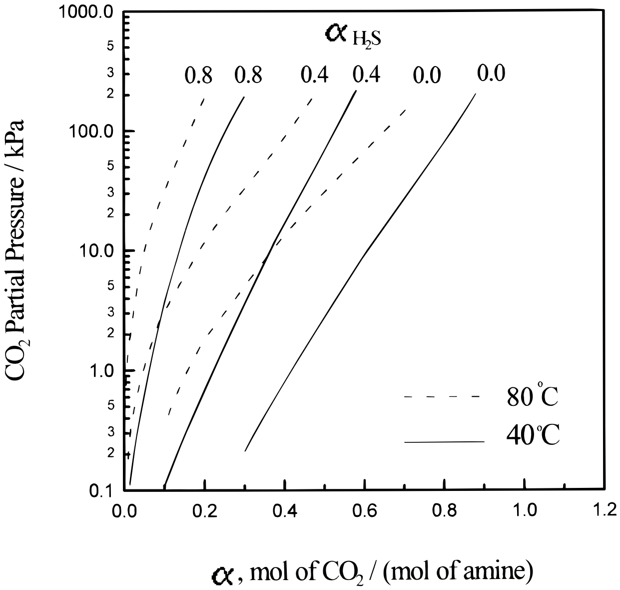

Figure 7. Partial pressures of CO_2 in 12 mass % DEA + 18 mass % AMP aqueous solution at 40 and 80 °C. The lines show the values calculated by the model of Deshmukh and Mather: solid lines, 40 °C; dashed lines, 80 °C.

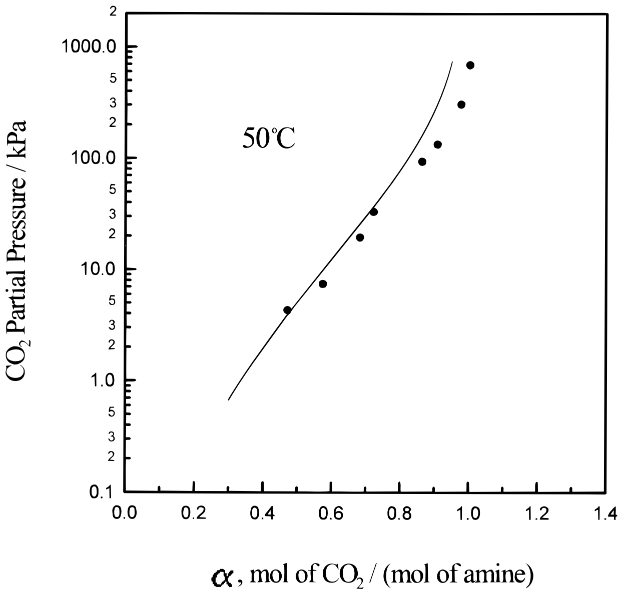

Figure 8. Comparison of the predicted and the observed solubility of the CO_2 in a 3.43 mol/L AMP aqueous solution at 50 °C. Points: data reported by Teng and Mather (1989). The lines show the values calculated by the model of Deshmukh and Mather.

In Figure 7, the calculated, using the model of Deshmukh and Mather, partial pressures of CO_2 over 12 mass % DEA + 18 mass % AMP aqueous solution at 40 and 80 °C are shown. The difference of CO_2 solubility between two temperatures 40 and 80 °C decreases as the H_2S loading capacity increases. At a particular partial pressure of CO_2, the effect of the higher temperature and the higher loading capacity of H_2S will lead to the loading of CO_2 during the solution decrease.

To test the applicability of the model, calculations for the systems not included in the data base have also been

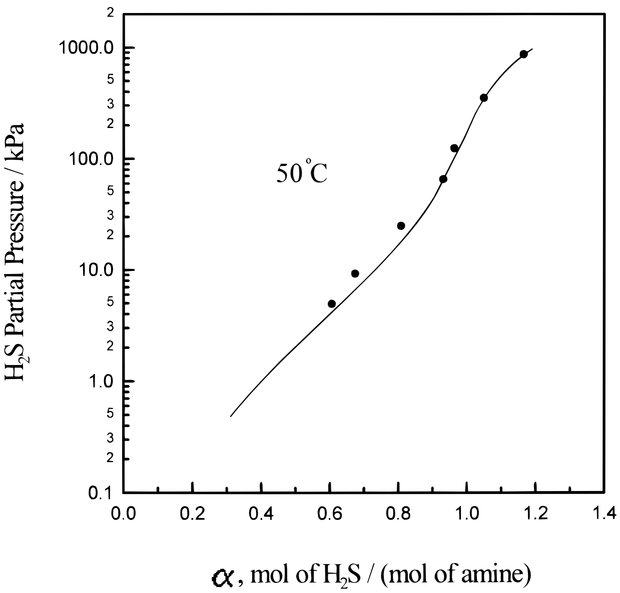

Figure 9. Comparison of the predicted and the observed solubility of the H_2S in a 3.43 mol/L AMP aqueous solution at 50 °C. Points: data reported by Teng and Mather (1989). The lines show the values calculated by the model of Deshmukh and Mather.

performed. The solubilities of CO_2 in a 3.43 mol/L AMP aqueous solution at 50 °C (data of Teng and Mather (1989)) and at partial pressures of acid gases less than 700 kPa are calculated using the model of Deshmukh and Mather. Except at the partial pressures of CO_2 beyond 300 kPa, the model yields satisfactory results for the partial pressures of CO_2 in 3.43 mol/L AMP, as shown in Figure 8. Figure 9 gives a comparison between the results of calculated and experimental solubilities of H_2S in 3.43 mol/L AMP aqueous solution at 50 °C (data of Teng and Mather (1989)). The results of the model calculations are satisfactory, as shown in Figure 9.

Conclusion

The solubilities of mixtures of carbon dioxide and hydrogen sulfide in $H_2O + DEA + AMP$ have been measured at 40 and 80 °C and at partial pressures of acid gases ranging from 1.0 to 200 kPa. The ternary mixtures studied were 30 mass % AMP, 6 mass % DEA + 24 mass % AMP, 12 mass % DEA + 18 mass % AMP, 18 mass % DEA + 12 mass % AMP, 24 mass % DEA + 6 mass % AMP, and 30 mass % DEA aqueous solutions. The model of Deshmukh and Mather has been used to represent the solubility of mixtures of CO_2 and H_2S in the ternary solutions. The model reasonably reproduces the equilibrium partial pressures of CO_2 and H_2S above the ternary solutions for the systems tested.

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