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

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The solubilities of mixtures of carbon dioxide and hydrogen sulfide in water + monoethanolamine (MEA) + 2-amino-2-methyl-1-propanol (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 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP and 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP aqueous solutions. The Kent and Eisenberg model has been modified 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

Solutions of amines are frequently used in gas treating processes to remove acid gases such as CO_2 and H_2S from gas streams in the natural gas and synthetic ammonia industries and petroleum chemical plants. Recently the use of blended amines such as mixtures of monoethanolamine (MEA) and *N*-methyldiethanolamine (MDEA) has been suggested for CO_2 removal (Chakravarty et al., 1985). Sterically hindered alkanolamines have also been proposed as commercially attractive solvents for removal of acid gases from gaseous streams (Sartori and Savage, 1983). Compared to MDEA, 2-amino-2-methyl-1-propanol (AMP) has the same CO_2 loading capacity (1 mol of CO_2/mol of amine) but has a higher reaction rate constant for the reaction with CO_2 (Li and Chang, 1994a). The H_2O + MEA + AMP may be considered as a new solvent in addition to H_2O + MEA + MDEA for the acid gas treating process. It is the purpose of this research to measure the solubility of mixtures of CO_2 and H_2S in H_2O + MEA + AMP.

Experimental Section

The materials, vapor−liquid equilibrium apparatus, and methods of analysis are the same as those used in our previous work (Li and Chang, 1994a). The loading capacity of the acid gases of solutions was determined by the titration method, similar to that of Teng and Mather (1989). The estimated experimental error in the measured solubility is about ±2−3%.

Results and Discussion

For the measurements of the solubility of mixtures of CO_2 and H_2S in H_2O + MEA + AMP, the systems studied were 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP and 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP aqueous solutions. The measured solubilities at 40 and 80 °C are presented in Tables 1−4. 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 acid gases. When two acid gases coexist in a system, the solubility of one of the acid gases will normally be affected and compete with that of the other acid gas.

Table 1. Solubility of Mixtures of CO_2 and H_2S in 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP Aqueous Solution at 40 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
0.895	25.59	0.209	0.459
1.351	8.219	0.351	0.207
1.561	21.78	0.268	0.363
1.856	1.148	0.442	0.048
6.212	66.41	0.239	0.467
9.222	2.989	0.516	0.049
15.98	27.75	0.409	0.200
21.51	112.8	0.266	0.445
27.27	128.4	0.280	0.442
33.75	6.044	0.538	0.046
38.43	45.49	0.456	0.193
80.34	61.32	0.497	0.170
95.58	11.05	0.582	0.043
120.3	62.79	0.510	0.146
138.1	12.84	0.598	0.041
148.8	22.73	0.587	0.054

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

Table 2. Solubility of Mixtures of CO_2 and H_2S in 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP Aqueous Solution at 80 °C

P/kPa		α[a]	
CO_2	H_2S	CO_2	H_2S
0.695	17.89	0.116	0.294
1.174	1.192	0.275	0.046
1.265	27.46	0.137	0.334
1.555	4.035	0.247	0.097
2.462	42.39	0.144	0.370
3.503	6.068	0.287	0.092
4.690	62.58	0.162	0.397
9.996	3.303	0.397	0.039
12.00	84.02	0.190	0.390
12.30	10.42	0.342	0.092
26.04	105.5	0.242	0.365
39.61	6.636	0.430	0.041
49.23	20.05	0.417	0.085
75.56	8.94	0.501	0.038
104.9	25.18	0.467	0.076
121.9	10.38	0.496	0.034

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

It is difficult to use the solubility data directly from the measurements for design calculations. A correlation to represent the solubility of two acid gases in blended amine

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Table 3. Solubility of Mixtures of CO_2 and H_2S in 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP Aqueous Solution at 40 °C

P/kPa		α^a	
CO_2	H_2S	CO_2	H_2S
0.628	3.393	0.317	0.196
1.263	1.972	0.349	0.106
2.056	27.43	0.220	0.451
5.343	11.09	0.386	0.203
5.517	4.327	0.393	0.103
9.005	64.25	0.242	0.486
16.21	21.32	0.406	0.210
20.59	9.640	0.455	0.101
22.29	14.95	0.488	0.142
25.99	114.5	0.272	0.493
27.00	31.83	0.420	0.217
41.82	15.52	0.494	0.096
42.88	44.43	0.440	0.224
73.44	21.67	0.539	0.093
78.42	74.13	0.449	0.237
151.3	38.35	0.603	0.104

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

Table 4. Solubility of Mixtures of CO_2 and H_2S in 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP Aqueous Solution at 80 °C

P/kPa		α^a	
CO_2	H_2S	CO_2	H_2S
0.545	4.556	0.124	0.155
1.769	5.519	0.212	0.134
2.956	8.238	0.211	0.156
3.069	49.33	0.124	0.412
6.053	28.09	0.207	0.277
6.109	4.430	0.297	0.079
10.49	13.10	0.287	0.149
10.60	99.10	0.143	0.483
10.61	2.785	0.385	0.047
19.13	64.34	0.229	0.343
27.77	28.76	0.323	0.185
29.60	21.34	0.359	0.146
52.06	50.54	0.332	0.221
70.93	30.38	0.413	0.139
82.82	7.284	0.480	0.042
127.3	8.441	0.550	0.041

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

solutions is normally required for practical applications. In this study, the method of Kent and Eisenberg (1976) will be applied to correlate the solubility of mixtures of CO_2 and H_2S in H_2O + MEA + AMP solutions. Equations describing phase equilibrium for the system $CO_2 + H_2S + H_2O$ + MEA + AMP were presented in our previous work (Li and Chang, 1994a,b). As in the model of Kent and Eisenberg (1976), literature values for Henry's law constants and for equilibrium constants for reactions not involving amines are also used in this study. The equilibrium constants which govern the main amine reactions are assumed to be functions of temperature, amine concentration, and acid gas loading (Li and Shen, 1993). Using the least-squares fit to the equilibrium partial pressures of mixtures of CO_2 and H_2S in H_2O + MEA + AMP, the equilibrium constants were determined as follows:

$$K_{11} = \exp\{-9.75 - 3055.56/(T/\mathrm{K}) - 1.18313 \times 10^8/(T/\mathrm{K})^3 + 0.11\alpha_{H_2S} + 0.55\alpha_{H_2S}^{\ 2} - 6.93\alpha_{CO_2} + 23.45\alpha_{CO_2}^{\ 2} + 30.44\alpha_{H_2S}\alpha_{CO_2} + 3.69m_1/(\mathrm{kmol{\cdot}m^{-3}}) - 0.78[m_1/(\mathrm{kmol{\cdot}m^{-3}})]^2 - 1.01m_1/(\mathrm{kmol{\cdot}m^{-3}})m_2/(\mathrm{kmol{\cdot}m^{-3}}) + 0.93\ln[m_1/(\mathrm{kmol{\cdot}m^{-3}})]\} \quad (1)$$

$$K_{12} = \exp\{-3.93 - 12833/(T/\mathrm{K}) - 2.5034 \times 10^8/(T/\mathrm{K})^3 - 0.32\alpha_{H_2S} + 1.54\alpha_{H_2S}^{\ 2} + 2.5\alpha_{CO_2} - 1.94\alpha_{CO_2}^{\ 2} - 1.38\alpha_{H_2S}\alpha_{CO_2} + 15.84m_2/(\mathrm{kmol{\cdot}m^{-3}}) - 2.17[m_2/(\mathrm{kmol{\cdot}m^{-3}})]^2 - 0.13m_1/(\mathrm{kmol{\cdot}m^{-3}})m_2/(\mathrm{kmol{\cdot}m^{-3}}) - 12.23\ln[m_2/(\mathrm{kmol{\cdot}m^{-3}})]\} \quad (2)$$

$$K_2 = \exp\{-97.02 + 5316.67/(T/\mathrm{K}) - 20.576 \times 10^8/(T/\mathrm{K})^3 - 19.45\alpha_{CO_2} + 33.32\alpha_{CO_2}^{\ 2} - 4.13m_1/(\mathrm{kmol{\cdot}m^{-3}}) + 0.07[m_1/(\mathrm{kmol{\cdot}m^{-3}})]^2 - 0.58m_1/(\mathrm{kmol{\cdot}m^{-3}})m_2/(\mathrm{kmol{\cdot}m^{-3}}) + 8.26\ln[m_1/(\mathrm{kmol{\cdot}m^{-3}})]\} \quad (3)$$

m_1 and m_2 are the molarities of MEA and AMP, respectively, α is the acid gas loading capacity of the solutions, and K is in kmol·m^{-3}.

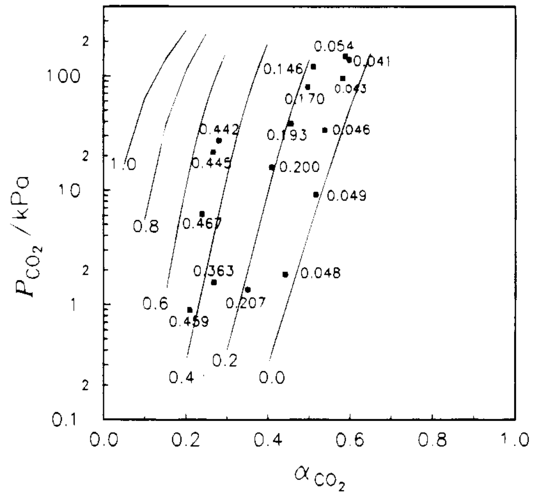

Figure 1. Effect of H_2S on the partial pressures of CO_2 over 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP aqueous solution at 40 °C. The specified value denotes H_2S loading of the solution. The lines show the values calculated by the modified Kent and Eisenberg model. The points show the data points.

The overall average absolute percentage deviation for the calculations of acid gas partial pressures is around 18%. Figure 1 shows the comparisons between calculated and experimental partial pressures of CO_2 over 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP aqueous solution at various H_2S loading capacities at 40 °C. The solubility of CO_2 over H_2O + MEA + AMP is affected by the solubility of H_2S in the solution; the 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 1.

A plot of the partial pressures of H_2S over 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP aqueous solution versus the H_2S loading of the solution at various CO_2 loading capacities at 40 °C is shown in Figure 2. The loading of H_2S of the solution is affected by the CO_2 loading of the solution. The lower the CO_2 loading capacity of the solution observed, the higher the H_2S loading capacity of the solution presented, as shown in Figure 2. The calculated solubilities of acid gases over H_2O + MEA + AMP by the modified Kent and Eisenberg model are generally in good agreement with experimental data as shown in Figures 1 and 2.

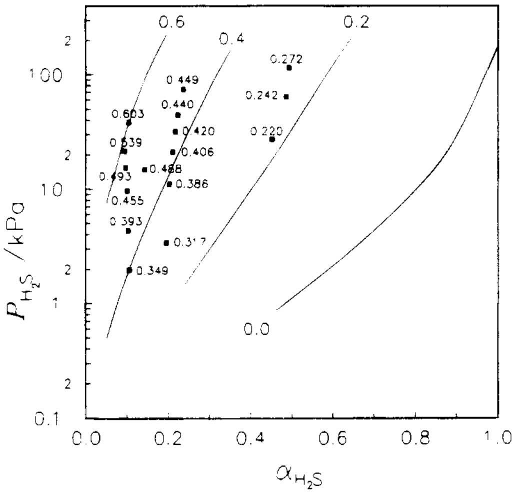

Figure 2. Effect of CO_2 on the partial pressures of H_2S over 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP aqueous solution at 40 °C. The specified value denotes CO_2 loading of the solution. The lines show the values calculated by the modified Kent and Eisenberg model. The points show the data points.

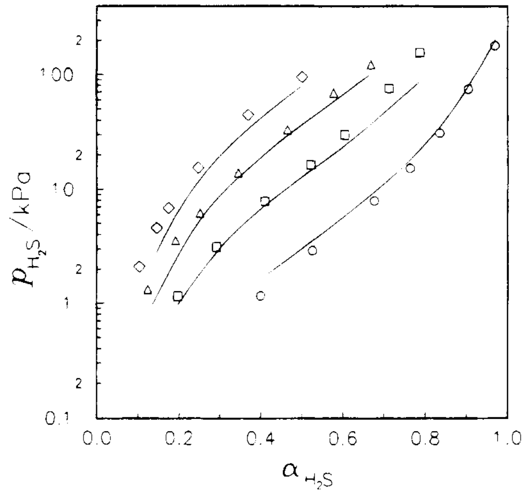

Figure 4. Partial pressure P of H_2S in 24 mass % MEA + 6 mass % AMP aqueous solution at various temperatures for various H_2S loadings. The lines show the values calculated by the modified Kent and Eisenberg model. The points show data reported by Li and Chang (1994a): ○, 40 °C; □, 60 °C; △, 80 °C; ◇, 100 °C.

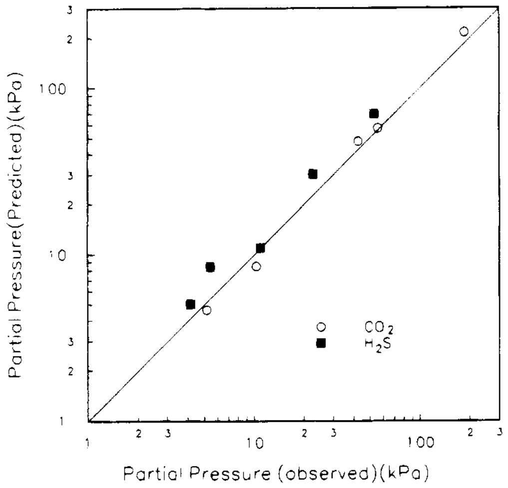

Figure 3. Comparison of the predicted and the observed solubilities of the mixtures of CO_2 and H_2S in a 3.43 mol/L AMP aqueous solution at 50 °C. The points show data reported by Teng and Mather (1989). The predicted values are calculated by the modified Kent and Eisenberg model.

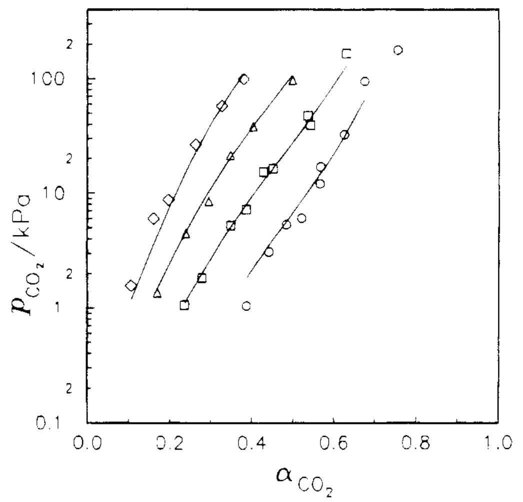

Figure 5. Partial pressure P of CO_2 in 6 mass % MEA + 24 mass % AMP aqueous solution at various temperatures for various CO_2 loadings. The lines show the values calculated by the modified Kent and Eisenberg model. The points show data reported by Li and Chang (1994b): ○, 40 °C; □, 60 °C; △, 80 °C; ◇, 100 °C.

To test the applicability of the model, calculations of the solution for data not included in the data base have also been performed. The solubilities of mixtures of CO_2 and H_2S 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 300 kPa are calculated using the modified Kent and Eisenberg model. The model yields satisfactory results for the partial pressures of mixtures of acid gases in H_2O + AMP, as shown in Figure 3. Figure 4 gives a comparison between the results of the calculated and experimental solubilities of H_2S in 24 mass % MEA + 6 mass % AMP aqueous solution for temperatures of 40–100 °C (data of Li and Chang (1994a)). The calculations of the solubility of CO_2 in 6 mass % MEA + 24 mass % AMP aqueous solution (data of Li and Chang (1994b)) were also carried out, and the results are shown in Figure 5. The results of the model calculations are satisfactory.

Conclusion

The solubilities of mixtures of CO_2 and H_2S in H_2O + MEA + AMP have been measured at 40 and 80 °C and at acid gas partial pressures up to 200 kPa. The systems studied were 3 kmol·m^{-3} MEA + 2 kmol·m^{-3} AMP and 2 kmol·m^{-3} MEA + 3 kmol·m^{-3} AMP aqueous solutions. The model of Kent and Eisenberg for calculating the solubilities of acid gases in alkanolamine solutions has been extended to represent the solubility of mixtures of CO_2 and H_2S in H_2S + MEA + AMP. The equilibrium constants of chemical reactions involving amines are expressed as functions of temperature, amine concentration, and acid gas loading. The model reasonably reproduces the equilibrium partial pressures of CO_2 and H_2S over H_2O + MEA + AMP for the systems tested. The model has also been tested for systems not included in the data base. Satisfactory results were obtained for the calculation of the solubility of H_2S (or CO_2) in H_2O + MEA + AMP solutions.

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