Solubility of Hydrogen Sulfide in Aqueous Mixtures of Monoethanolamine with *N*-Methyldiethanolamine

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The solubilities of hydrogen sulfide in aqueous mixtures of monoethanolamine (MEA) with *N*-methyldiethanolamine (MDEA) have been measured at 40, 60, 80, and 100 °C and at partial pressures of hydrogen sulfide ranging from 1.0 to 450 kPa. The mixtures of alkanolamines studied are 4.95 kmol m^{-3} MEA, 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA, 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA, and 2.57 kmol m^{-3} MDEA aqueous solutions. The solubilities of hydrogen sulfide in aqueous alkanolamine solutions are reported as functions of the partial pressure of hydrogen sulfide at the temperatures of 40–100 °C.

Introduction

Alkanolamine aqueous solutions are frequently used for the removal of acidic gases, such as CO_2 and H_2S, from gas streams in the natural gas and synthetic ammonia industries and petroleum chemical plants. Industrially important alkanolamine aqueous solutions are monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA) and *N*-methyldiethanolamine (MDEA). Aqueous MEA solutions have been widely used due to their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (*1*). Due to the formation of rather stable carbamates by primary (or secondary) amines with CO_2, the loading capacity of MEA cannot reach a value much beyond 0.5 mol of CO_2/mol of amine (*2*). For a gas stream that contains both CO_2 and H_2S, the aqueous MDEA solution is found to be an appropriate solution for the selective removal of H_2S from the gas stream (*3*, *4*). Advantages of the use of MDEA solutions include their high loading capacity (about 1.0 mol of CO_2/mol of amine) and low heat of reaction with the acid gases (*5*). The lower heat of reaction leads to lower energy requirements for regeneration. However, a low reaction rate of CO_2 with tertiary amines limits the use of MDEA solutions (*2*).

Recently the use of blended amines, a selection of two or more amines in varying compositions, brings about a considerable improvement in absorption and a great savings in energy requirements (*6*). The use of blended amines intends to combine the absorption characteristics of the constituent amines; advantages of the use of individual amine, such as the higher loading capacity and the faster reaction rate, are expected to contribute to the resulting solution. Blends of primary and tertiary amines, mixtures of MEA and MDEA, have been suggested to be used for CO_2 removal (*6*). Knowledge of the equilibrium solubility of acid gases such as CO_2 and H_2S in alkanolamine aqueous solutions is essential in the rational design of the gas absorption units for removing these acid gases from gas streams. The solubilities of CO_2 in aqueous mixtures of MEA and MDEA have been reported in the literature (*7–9*). For partial pressures of CO_2 below 315 kPa, solubilities of CO_2 in 2.0 kmol m^{-3} MEA + 2.0 kmol m^{-3} MDEA aqueous solution were studied experimentally at 40 and 80 °C (*7*). The solubilities of CO_2 in six MEA + MDEA + H_2O solutions were also reported for temperatures of 40–100 °C and for partial pressures of CO_2 up to 2000 kPa (*8*, *9*). However, the solubility of H_2S in MEA + MDEA + H_2O systems has not yet been reported in the literature. Thus, it is the purpose of this research to study experimentally the solubilities of H_2S in MEA + MDEA + H_2O systems at temperatures ranging from 40 to 100 °C. The systems selected are 4.95 kmol m^{-3} MEA (30 mass % MEA), 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA (24 mass % MEA + 6 mass % MDEA), 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA (12 mass % MEA + 18 mass % MDEA), and 2.57 kmol m^{-3} MDEA (30 mass % MDEA) aqueous solutions. The solubility data will be measured for partial pressures of H_2S up to 450 kPa.

Experimental Section

Two vapor–liquid equilibrium apparatus have been set up and tested in this study to make H_2S solubility measurements over the MEA + MDEA + H_2O solutions for partial pressures of H_2S ranging from 1 to 450 kPa. For partial pressures of H_2S above 200 kPa, the solubility of H_2S was measured in a stirred 0.5-L Zipperclave batch equilibrium cell. When the total pressure of the cell does not change for 2 h, the equilibrium is assumed to have been reached; it will normally take 5–6 h for the system to reach equilibrium. The H_2S partial pressure was obtained by substracting the partial pressure of water from the total pressure of the system. The partial pressure of water was obtained by using Raoult's law. The mole fractions of water in the systems studied are greater than 0.9 for most cases. Thus, using Raoult's law for the water content of the vapor phase is a reasonable approximation, and the error is expected to be negligible. The solubility (loading capacity) of H_2S in MEA + MDEA + H_2O systems was determined by using the titration method presented by Jou et al. (*10*). At equilibrium, the liquid sample was withdrawn from the cell into a vessel containing 1.0 M NaOH, thus converting free dissolved acid gas into the involatile ionic species. The H_2S content of the sample was determined by reacting the liquid with a solution of acidified 0.1 N I_2 (I^-). The unreacted I_2 was back-titrated with 0.1 N $Na_2S_2O_3$ using starch as the indicator.

A 1.0-L stainless steel vapor-recirculation equilibrium cell was used to measure the equilibrium solubility of H_2S in MEA + MDEA + H_2O systems for partial pressures of H_2S below 200 kPa. In the region of low H_2S partial pressures, nitrogen was introduced and mixed with H_2S, and the partial pressure of H_2S was determined by gas chromatography. When both the system pressure and the gas phase concentrations, determined by the gas chromatograph, do not vary for 2 h, the equilibrium is assumed to have been reached; it usually

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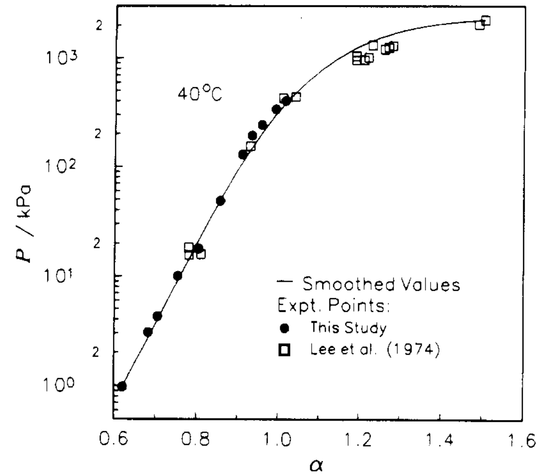

Figure 1. Partial Pressures P of H_2S in 2.5 kmol m^{-3} MEA aqueous solution at 40 °C for various loadings α (mol of H_2S/total mol of amine).

Table I. Partial Pressures P of H_2S in 2.5 kmol m^{-3} MEA Aqueous Solution at 40 °C for Loadings of H_2S, α (mol of H_2S/total mol of amine)

this study		Lee et al. (*11*)			
P/kPa	α	P/kPa	α	P/kPa	α
0.974	0.620	15.72	0.781	1020	1.220
3.051	0.682	16.00	0.810	1047	1.190
4.261	0.705	18.41	0.780	1214	1.260
10.06	0.754	154.4	0.930	1258	1.270
17.98	0.804	428.2	1.010	1305	1.280
48.54	0.857	439.9	1.040	1323	1.230
129.5	0.910	959.7	1.190	2049	1.490
194.0	0.934	968.7	1.210	2253	1.505
243.1	0.958				
337.2	0.992				
405.1	1.016				

takes 4–5 h for the system to reach equilibrium. The partial pressure of H_2S was obtained from the pressure of the system and the gas-phase analysis. The vapor–liquid equilibrium apparatus and experimental procedures are essentially the same as described in our previous work on the solubility of CO_2 in MEA + MDEA + H_2O systems (*8*). MEA is Riedel-de Haën reagent grade with a 99% purity, and MDEA is Riedel-de Haën reagent grade with a 98.5% purity. Alkanaolamine aqueous solutions were prepared from distilled water. The experimental error in the solution H_2S loading (mol of H_2S/mol of total amine) is estimated to be ±2–3%.

Results and Discussion

To test the vapor–liquid equilibrium apparatus and to confirm the sampling and analytical procedures, we have obtained data for the system for which data are available in the literature. Solubilities of H_2S in 2.5 kmol m^{-3} MEA aqueous solution have been reported at 40 °C (*11*). The results of the solubilities measured in this study along with the literature values are presented in Table I. Using the least-squares fit of all data points to a polynomial equation, a solid curve, as shown in Figure 1, is determined. The determined equation is as follows:

$$\ln (P/\text{kPa}) = 0.4073 - 21.75\alpha + 33.67\alpha^2 + 12.09\alpha^3 - 13.96\alpha^4 - 12.43\alpha^5 + 7.762\alpha^6 \quad (1)$$

Table II. Partial Pressures P of H_2S in 4.95 kmol m^{-3} MEA Aqueous Solution for Loadings of H_2S, α (mol of H_2S/total mol of amine)

40 °C		60 °C		80 °C		100 °C	
P/kPa	α	P/kPa	α	P/kPa	α	P/kPa	α
1.635	0.556	0.963	0.478	3.124	0.296	1.159	0.135
3.177	0.579	3.191	0.510	6.198	0.333	1.826	0.143
5.670	0.624	9.237	0.558	14.31	0.357	4.229	0.169
13.46	0.668	11.88	0.568	26.69	0.425	10.17	0.209
23.89	0.707	23.57	0.627	69.29	0.534	20.00	0.272
69.18	0.780	55.17	0.681	125.5	0.631	46.01	0.393
131.6	0.795	121.3	0.744	230.5	0.692	69.29	0.441
236.5	0.824	184.4	0.769	293.3	0.739	132.2	0.530
316.3	0.847	222.1	0.782	322.2	0.736	218.8	0.606
380.3	0.866	330.0	0.810	415.9	0.778	285.3	0.639
435.3	0.899	409.7	0.833			367.9	0.706

Table III. Partial Pressures P of H_2S in 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA Aqueous Solution for Loadings of H_2S, α (mol of H_2S/total mol of amine)

40 °C		60 °C		80 °C		100 °C	
P/kPa	α	P/kPa	α	P/kPa	α	P/kPa	α
1.455	0.345	1.532	0.244	1.551	0.163	1.285	0.130
2.813	0.414	1.934	0.246	1.930	0.164	2.383	0.136
4.434	0.484	4.013	0.323	4.180	0.199	4.365	0.157
8.033	0.562	7.641	0.406	8.368	0.293	8.427	0.189
17.50	0.670	17.21	0.512	22.91	0.410	16.70	0.252
42.86	0.757	34.41	0.605	42.83	0.502	28.97	0.307
154.5	0.825	81.64	0.708	73.56	0.594	50.92	0.381
222.9	0.870	184.9	0.782	131.3	0.658	91.01	0.461
288.1	0.872	245.6	0.812	189.8	0.680	155.2	0.538
382.6	0.876	306.2	0.822	295.0	0.753	264.5	0.593
444.6	0.886	440.1	0.843	398.9	0.781	363.2	0.676

Table IV. Partial Pressures P of H_2S in 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA Aqueous Solution for Loadings of H_2S, α (mol of H_2S/total mol of amine)

40 °C		60 °C		80 °C		100 °C	
P/kPa	α	P/kPa	α	P/kPa	α	P/kPa	α
1.309	0.291	1.399	0.198	1.307	0.132	1.365	0.103
2.359	0.349	2.636	0.247	2.988	0.155	2.773	0.115
3.657	0.422	6.054	0.326	7.275	0.229	2.907	0.116
9.424	0.558	10.04	0.390	8.915	0.253	3.398	0.120
19.96	0.650	18.27	0.482	16.63	0.324	4.336	0.127
76.61	0.802	33.56	0.577	29.78	0.409	6.962	0.147
172.7	0.866	71.50	0.704	59.13	0.511	15.13	0.207
253.8	0.878	153.7	0.781	109.0	0.624	32.89	0.301
318.0	0.899	263.9	0.829	271.1	0.741	66.26	0.400
379.8	0.913	387.2	0.855	368.3	0.779	112.9	0.479
434.4	0.950	442.3	0.881			192.8	0.514
						275.2	0.594
						379.4	0.637

where P is the H_2S partial pressure and α is the loading in terms of moles of H_2S per mole of amine. A comparison of the results is also shown graphically in Figure 1. As can be seen from Figure 1, the data of Lee et al. (*11*) exhibit a little scatter near the H_2S partial pressure of 1000 kPa. Generally the solubility data measured in this study are in good agreement with the literature values (*11*).

The blended amine systems studied are 4.95 kmol m^{-3} MEA, 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA, 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA, and 2.57 kmol m^{-3} MDEA aqueous solutions. The solubilities of H_2S in MEA + MDEA + H_2O systems at 40, 60, 80, and 100 °C are presented in Tables II–V. Plots of the partial pressures of H_2S as functions of the loading of H_2S are given in Figures 2–5. As can be seen from Figures 2–5, the higher the H_2S partial pressure, the higher the loading capacity of H_2S in solution observed. As for the temperature effect, the solubility of H_2S varies systematically with temperature; the lower the temperature, the higher the H_2S loading obtained. When compared with the solubility of H_2S in 2.57 kmol m^{-3} MDEA, the solubility of H_2S in 4.95 kmol m^{-3} MEA is found to be more temperature-dependent at the lower H_2S partial pressure region and less temperature-dependent at the higher H_2S partial pressures, as shown in Figures 2 and 5.

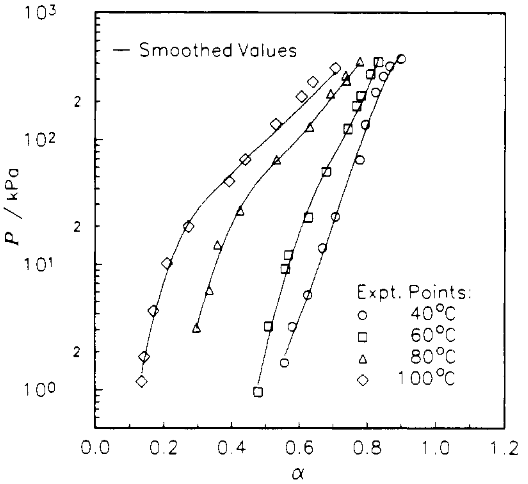

Figure 2. Partial pressures P of H_2S in 4.95 kmol m^{-3} MEA aqueous solution at various temperatures for various loadings α (mol of H_2S/total mol of amine).

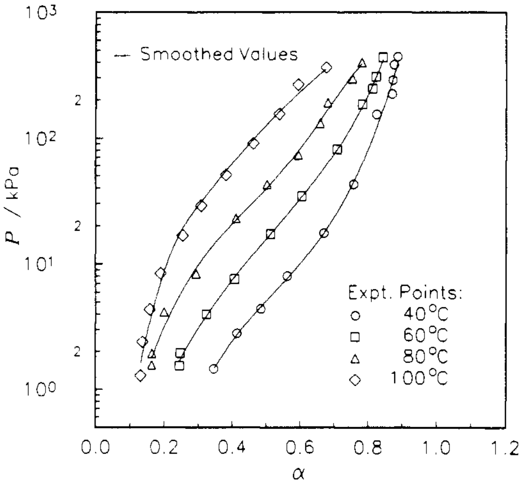

Figure 3. Partial pressures P of H_2S in 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA aqueous solution at various temperature for various loadings α (mol of H_2S/total mol of amine).

Table V. Partial Pressures P of H_2S in 2.57 kmol m^{-3} MDEA Aqueous Solution for Loadings of H_2S, α (mol of H_2S/total mol of amine)

40 °C		60 °C		80 °C		100 °C	
P/kPa	α	P/kPa	α	P/kPa	α	P/kPa	α
3.331	0.230	3.767	0.180	2.161	0.113	1.498	0.082
4.100	0.266	5.750	0.195	3.413	0.137	2.510	0.086
5.816	0.315	8.166	0.230	7.461	0.151	3.846	0.108
8.206	0.360	13.39	0.291	12.36	0.166	10.00	0.123
14.04	0.440	28.57	0.416	21.52	0.211	20.11	0.163
29.17	0.585	50.60	0.530	43.18	0.339	40.74	0.244
59.46	0.705	97.58	0.642	91.23	0.473	90.13	0.357
128.2	0.800	160.2	0.716	153.1	0.560	131.9	0.383
229.6	0.855	235.9	0.754	210.6	0.598	191.0	0.446
330.6	0.887	332.3	0.792	371.5	0.644	295.5	0.481
445.7	0.902			426.5	0.667	348.0	0.515

To investigate the effects of amine concentrations on the loading of H_2S, plots of the H_2S partial pressures versus H_2S loading for four amine aqueous solutions at 40 and 100 °C are shown in Figures 6 and 7, respectively. As shown in Figure 6, the loadings of H_2S in 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA are larger than those values in 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA at the region of low partial pressures of H_2S; the loadings of H_2S in two solutions cross over at the partial pressure of H_2S near 70 kPa. At 40 °C for H_2S partial pressures below 40 kPa, the H_2S loadings in both 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA and 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA are between those values in 4.95 kmol m^{-3} MEA and in 2.57 kmol m^{-3} MDEA, as shown in Figure 6. However, it is noted that the H_2S solubilities in 2.0 kmol

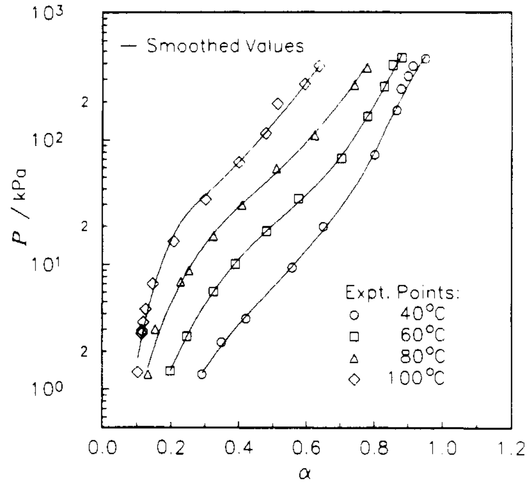

Figure 4. Partial pressures P of H_2S in 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA aqueous solution at various temperatures for various loadings α (mol of H_2S/total of amine).

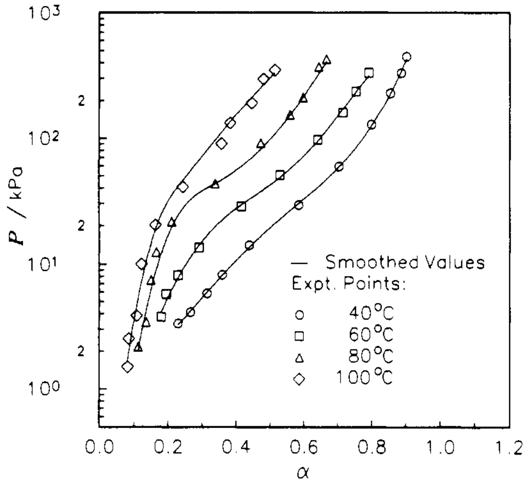

Figure 5. Partial pressures P of H_2S in 2.57 kmol m^{-3} MDEA aqueous solution at various temperatures for various loadings α (mol of H_2S/total mol of amine).

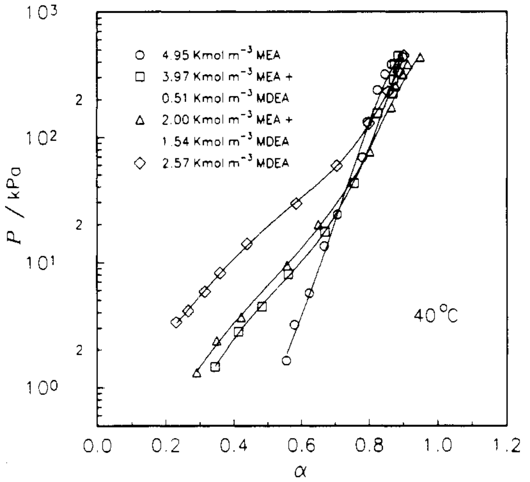

Figure 6. Partial pressures P of H_2S in various MEA + MDEA aqueous solutions at 40 °C for various loadings α (mol of H_2S/total mol of amine).

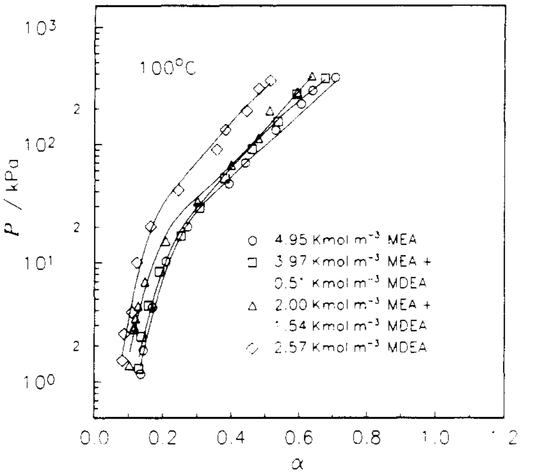

Figure 7. Partial pressures P of H_2S in various MEA + MDEA aqueous solutions at 100 °C for various loadings α (mol of H_2S/total mol of amine).

m^{-3} MEA + 1.54 kmol m^{-3} MDEA are higher than those values in both 4.95 kmol m^{-3} MEA and 2.57 kmol m^{-3} MDEA for H_2S partial pressures above 40 kPa at 40 °C. At 100 °C, H_2S solubilities vary systematically from 4.95 kmol m^{-3} MEA, to 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA, to 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA, and 2.57 kmol m^{-3} MDEA. For the same H_2S partial pressure, the 4.95 kmol m^{-3} MEA aqueous solution yields a higher H_2S solubility than the 2.57 kmol m^{-3} MDEA aqueous solution.

Conclusion

The solubilities of H_2S in blended mixtures of MEA and MDEA have been reported at 40–100 °C and at H_2S partial pressures up to 450 kPa. The systems studied are 4.95 kmol m^{-3} MEA, 3.97 kmol m^{-3} MEA + 0.51 kmol m^{-3} MDEA, 2.0 kmol m^{-3} MEA + 1.54 kmol m^{-3} MDEA, and 2.57 kmol m^{-3} MDEA aqueous solutions. Solubilities of H_2S in 2.5 kmol m^{-3} MEA aqueous solution at 40 °C have also been measured; the data obtained in this study are generally in good agreement with the data reported in the literature.

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