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Solubility of Mixtures of Hydrogen Sulfide and Carbon Dioxide in Aqueous *N*-Methyldiethanolamine Solutions[†]

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The solubilities of mixtures of hydrogen sulfide and carbon dioxide in a 35 wt % (3.04 kmol/m^3) aqueous solution of *N*-methyldiethanolamine at 40 and 100 °C have been measured. Partial pressures of the acid gases ranged from 0.006 to 101 kPa at 40 °C and from 4 to 530 kPa at 100 °C.

Introduction

Aqueous solutions of alkanolamines are commonly used to strip acid gases (H_2S and CO_2) from streams contaminated with these components. The two most widely used amines are monoethanolamine (MEA) and diethanolamine (DEA). Other amines, which have different physical properties, are also being explored as potential solvents in the stripping processes.

N-Methyldiethanolamine (MDEA) solutions are used for the selective removal of H_2S from gas streams which contain both CO_2 and H_2S. The use of MDEA solutions was first described by Frazier and Kohl (*1*). In addition to its selectivity, MDEA has a lower enthalpy of reaction with the acid gases and a lower vapor pressure of the solution than primary and secondary amines like MEA and DEA. The smaller enthalpy of reaction leads to lower energy requirements for regeneration while the lower vapor pressure results in smaller losses of solvent by vaporization. Another advantage of MDEA is that it does not degrade readily; that is, it does not react irreversibly to form compounds that accumulate in the solution. Riesenfeld and Brocoff (*2*) have reviewed the application of MDEA in gas processing and indicated that its use is growing.

Savage et al. (*3*) have shown that the selectivity of MDEA for H_2S is mainly due to a kinetic effect and that the equilibrium selectivity is small. They obtained data on the simultaneous absorption of H_2S and CO_2 in an MDEA solution. Their results show that the rate of reaction of H_2S was much faster than that for CO_2. Haimour and Sandall (*4*) have also measured the rate of reaction of CO_2 in MDEA solutions.

In this paper, new data are presented for the vapor–liquid equilibrium in the system H_2S–CO_2–MDEA–H_2O.

Previous Work

Table I summarizes the previous experimental studies for the solubility of carbon dioxide in aqueous solutions of MDEA. Those for hydrogen sulfide are in Table II.

The only other experimental investigation of the solubility of mixtures of H_2S and CO_2 was that of Ho and Eguren (*5*). They measured the solubility of the mixture at 40 and 100 °C in a 49 wt % MDEA solution.

Experimental Apparatus and Procedure

Well-established methods and equipment were employed to obtain the new data. The experimental apparatus and procedure are the same as those detailed in Jou et al. (*6*). Thus, the experiment will only be described here briefly.

Table I. Experimental Investigations of the Solubility of Carbon Dioxide in Aqueous Solutions of MDEA

source	MDEA concn (kmol/m^3)	temp (°C)	CO_2 partial pressure (kPa)
Jou et al. (*8*)	2.0	25	0.001–6380
	2.0	40	0.002–6630
	2.0	70	0.002–6020
	2.0	100	0.05–5530
	2.0	120	0.07–5530
	4.28	25	0.004–6370
	4.28	40	0.002–6570
	4.28	70	0.002–6280
	4.28	100	0.04–5590
	4.28	120	0.14–5290
Bhairi (*9*)	1.0	25	14–2050
	1.73	37.8	19–4970
	1.73	65.6	29–5870
	1.73	115.6	87–6160
	2.0	25	11–4870
	2.0	50	44–4650
Ho and Eguren (*5*)	2.0	40	3400–5700
	2.0	50	3300–6500
	4.38	40	0.009–0.9
Austgen et al. (*10*)	2.0	40	0.006–93
	4.28	40	0.01–94
MacGregor and Mather (*11*)	2.0	40	1–3770
Jou et al. (*6*)	3.04	40	0.004–100
	3.04	100	1.0–262
Shen and Li (*12*)	2.6	40	1.2–2000
	2.6	60	1.1–2000
	2.6	80	1.7–1200
	2.6	100	3.0–1900

Basically, the apparatus consisted of an equilibrium cell equipped with large windows such that its contents could be easily observed. A pump was used to circulate a portion of the vapor from the top of the cell into the bottom and thus the liquid phase. The cell and the pump were housed in a temperature-controlled air bath. The pressure in the cell was measured using Heise gauges, which had been calibrated against a dead-weight gauge. The gauges have an accuracy of ±0.1% of full-scale span. The temperature was monitored by using an iron–constantan thermocouple. The temperature of the experimental fluids was measured to better than 0.5 °C.

Samples were taken of both phases. The vapor phase was analyzed using gas chromatography. Liquid samples were withdrawn from the equilibrium cell into a vessel containing 1 kmol/m^3 NaOH, thus converting free dissolved acid gas into the involatile ionic species. The CO_2 content in an aliquot of the liquid sample was determined by adding excess 0.1

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Table II. Experimental Investigations of the Solubility of Hydrogen Sulfide in Aqueous Solutions of MDEA

source	MDEA concn (kmol/m^3)	temp (°C)	H_2S partial pressure (kPa)
Jou et al. (*8*)	1.0	25	0.006–1960
	1.0	40	0.002–2730
	1.0	70	0.002–5030
	1.0	100	0.09–5890
	1.0	120	0.05–5230
	2.0	40	0.003–2260
	2.0	100	0.75–1550
	4.28	25	0.006–1960
	4.28	40	0.003–2800
	4.28	70	0.001–4990
	4.28	100	0.04–5840
	4.28	120	0.34–5230
Bhairi (*9*)	1.0	25	16–1280
	1.73	37.8	14–1360
	1.73	65.6	13–1540
	1.73	115.6	35–1270
MacGregor and Mather (*11*)	2.0	40	0.52–1600
Jou et al. (*6*)	3.04	40	0.002–313
	3.04	100	0.55–302
	4.39	40	0.06–5.9

kmol/m^3 $BaCl_2$ to precipitate the carbonate as $BaCO_3$. The precipitate was titrated with standardized 0.1 kmol/m^3 HCl. The H_2S content in an aliquot of the sample was determined by reacting the liquid with acidified 0.1 kmol/m^3 I_2. The unreacted I_2 was back-titrated with 0.1 kmol/m^3 $Na_2S_2O_3$. The experimental error in the solution loading is estimated to be better than 3% in the range studied.

The MDEA was obtained from Aldrich and is 99+% pure. The H_2S is Matheson CP Grade (99.6+% pure), and the CO_2 was supplied by Linde (99.99+% pure). These components were used without further purification. The water was laboratory distilled. Certified solutions of iodine and sodium thiosulfate, which were used in the iodometric titrations, were obtained from Fisher Scientific. The iodine was 0.1000 ± 0.0005 kmol/m^3, and the thiosulfate was 0.1000 ± 0.0002 kmol/m^3.

Results

The measured solubilities for various mixtures of hydrogen sulfide and carbon dioxide in 35 wt % MDEA at 40 °C are presented in Table III. At this temperature the H_2S partial pressures were from 0.3 to 101 kPa and the CO_2 partial pressures from 0.006 to 101 kPa. The measured solubilities at 100 °C are listed in Table IV. At 100 °C, the partial pressure

Table III. Solubility of H_2S + CO_2 Mixtures in 35 wt % MDEA Solution at 40 °C

partial pressure (kPa)		mole ratio in liquid (mol/mol)		partial pressure (kPa)		mole ratio in liquid (mol/mol)	
H_2S	CO_2	H_2S/MDEA	CO_2/MDEA	H_2S	CO_2	H_2S/MDEA	CO_2/MDEA
3.70	23.9	0.0769	0.523	10.19	0.719	0.366	0.0205
2.45	15.1	0.0678	0.399	9.70	1.099	0.353	0.0307
2.51	11.0	0.0784	0.316	10.46	1.207	0.355	0.0318
0.122	0.976	0.0161	0.00813	10.42	1.618	0.352	0.0388
0.258	0.919	0.0356	0.0726	10.92	3.271	0.339	0.0775
8.38	0.0361	0.448	0.00101	11.56	2.824	0.358	0.0673
2.07	0.014	0.146	0.00061	10.85	3.417	0.343	0.0836
4.30	0.00621	0.215	0.00044	11.25	4.213	0.341	0.102
1.61	0.0151	0.143	0.00076	16.97	14.53	0.355	0.249
1.06	0.0174	0.104	0.00077	18.72	19.09	0.331	0.291
0.734	0.0188	0.0847	0.00129	17.46	20.46	0.310	0.310
0.437	0.0144	0.0605	0.00074	15.33	14.88	0.321	0.260
0.348	0.0727	0.0535	0.00668	16.68	13.17	0.346	0.226
0.415	0.0796	0.064	0.00819	13.23	8.695	0.338	0.168
1.24	0.120	0.103	0.00659	2.71	0.457	0.200	0.0273
1.15	0.0498	0.108	0.00248	3.16	0.719	0.197	0.0324
10.4	0.228	0.36	0.00654	3.85	1.35	0.204	0.0533
12.9	0.193	0.49	0.00680	5.00	2.16	0.236	0.0756
48.9	0.14	0.699	0.00179	5.14	2.67	0.230	0.0908
76.6	0.264	0.811	0.00259	4.50	3.19	0.214	0.112
100.0	0.262	0.888	0.00086	5.19	3.95	0.219	0.127
97.1	0.661	0.873	0.00452	5.47	5.44	0.209	0.164
98.0	2.50	0.873	0.0114	4.41	5.45	0.193	0.178
5.12	1.05	0.266	0.047	5.84	7.81	0.209	0.218
59.1	1.02	0.746	0.0126	6.01	9.34	0.208	0.252
86.6	9.4	0.815	0.0489	4.90	9.42	0.177	0.270
68.8	33.8	0.650	0.194	6.50	9.51	0.222	0.242
31.8	70.2	0.304	0.516	4.91	7.65	0.192	0.237
13.9	88.8	0.127	0.649	3.32	4.61	0.149	0.199
6.34	97.4	0.0863	0.758	3.91	4.17	0.161	0.184
1.21	33.7	0.049	0.588	0.139	28.7	0.00351	0.594
0.644	18.1	0.0406	0.455	0.609	28.9	0.0118	0.591
0.587	9.08	0.0553	0.375	4.49	39.0	0.0623	0.612
2.09	3.43	0.160	0.154	4.17	21.7	0.0836	0.506
7.88	2.16	0.341	0.0958	2.81	14.3	0.076	0.42
53.4	1.65	0.715	0.0201	8.12	31.9	0.117	0.539
101.0	0.0978	0.882	0.0007	4.99	24.1	0.0947	0.537
71.3	0.154	0.805	0.00144	2.92	16.9	0.0752	0.498
27.5	0.0153	0.583	0.00021	1.06	7.55	0.0473	0.342
6.51	0.00506	0.303	0.00017	1.52	9.43	0.0584	0.349
2.96	0.02790	0.194	0.00118	3.46	20.3	0.0865	0.599
0.233	0.01030	0.047	0.00093	7.68	91.5	0.0702	0.709
0.0641	0.00559	0.0241	0.00118	5.92	89.7	0.0525	0.679
0.0323	0.0227	0.0167	0.00554	3.28	53.3	0.0435	0.658
0.0401	0.111	0.0166	0.021	2.00	33.7	0.0369	0.556
0.743	101.0	0.0101	0.788				

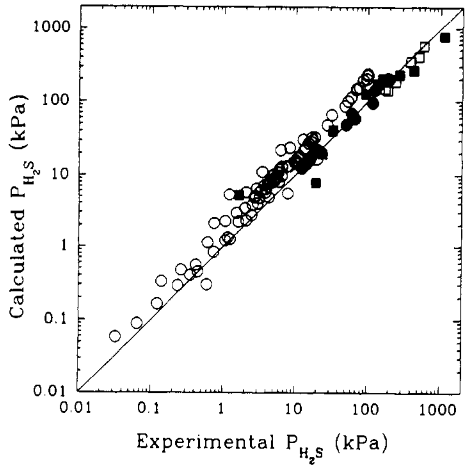

Figure 1. A comparison of the partial pressure of hydrogen sulfide predicted with the Deshmukh–Mather correlation and the experimental values for mixtures of hydrogen sulfide and carbon dioxide (this work, (○) 40 °C, (□) 100 °C; Ho and Eguren (*5*), (●) 40 °C, (■) 100 °C).

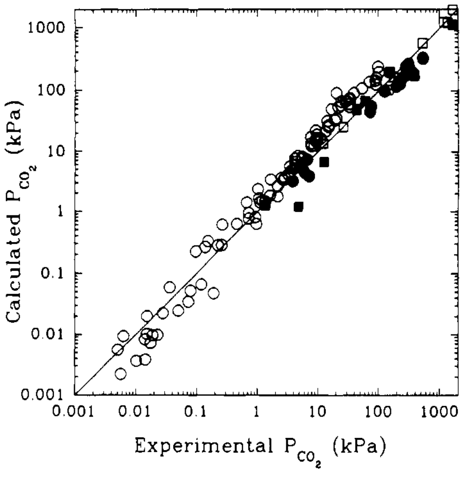

Figure 2. A comparison of the partial pressure of carbon dioxide predicted with the Deshmukh–Mather correlation and the experimental values for mixtures of carbon dioxide and hydrogen sulfide (this work, (○) 40 °C, (□) 100 °C; Ho and Eguren (*5*), (●) 40 °C, (■) 100 °C).

Table IV. Solubility of H_2S + CO_2 Mixtures in 35 wt % MDEA Solution at 100 °C

partial pressure (kPa)		mole ratio in liquid (mol/mol)	
H_2S	CO_2	H_2S/MDEA	CO_2/MDEA
20.3	3.84	0.147	0.0078
12.2	5.54	0.105	0.016
60.2	6.00	0.268	0.006
15.8	6.65	0.118	0.02
126.0	7.13	0.386	0.0035
12.4	72.8	0.075	0.098
50.4	76.1	0.193	0.077
61.8	125	0.213	0.111
16.9	196	0.079	0.172
14.0	225	0.060	0.191
67.0	257	0.178	0.172
196	281	0.367	0.150
190	306	0.365	0.161
22.9	367	0.071	0.235
118	529	0.210	0.244

of H_2S ranged from 12 to 200 kPa and the CO_2 partial pressure from 4 to 530 kPa.

The experimental data for mixtures were then compared with predictions using the Deshmukh–Mather correlation (*6*, *7*). Using the experimental loadings, the equilibrium partial pressures of hydrogen sulfide and carbon dioxide were predicted. Figure 1 shows the predicted H_2S partial pressure versus the experimental values. Figure 2 is a similar plot for CO_2. The values of Ho and Eguren (*5*) are in agreement with the present work and with the predictions of the model.

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