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Solubility of Mixtures of Hydrogen Sulfide and Carbon Dioxide in Aqueous Solutions of Triethanolamine

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The solubility of mixtures of hydrogen sulfide and carbon dioxide in three triethanolamine solutions, (2.0, 3.5, and 5.0) mol dm^{-3}, has been determined at temperatures of 50 °C, 75 °C, and 100 °C at partial pressures up to 5490 kPa.

Aqueous alkanolamine solutions are commonly used for the removal of H_2S and CO_2 from natural gas streams. Triethanolamine (TEA) solutions were initially used, but they were superseded by monoethanolamine and diethanolamine solutions which have a higher rate of reaction with the acid gases (Gregory and Scharmann, 1937). Van den Berg (1962) investigated the use of TEA solutions for the removal of CO_2 from apple storage chambers. The use of triethanolamine solutions in a dual solvent process has been proposed by Strelzoff (1970). The gas stream is contacted with a triethanolamine solution to remove the bulk of the carbon dioxide. By reduction of the pressure, about half of the absorbed carbon dioxide is liberated from the solution without the need for heating. The partially purified gas from the TEA absorber is sent to a second stage absorber where the carbon dioxide content is reduced to less than 0.05% using a solution of monoethanolamine. Recently, interest has been shown in the use of TEA for bulk removal of CO_2 and in the selective removal of H_2S. Goddin (1982) has shown that TEA bulk removal combined with membrane permeation resulted in the lowest cost removal of CO_2 from gases used for enhanced oil recovery. Sotelo et al. (1990) have measured the kinetics of the absorption of CO_2 by TEA solutions, and Linek et al. (1990) have simulated the design and operation of an industrial absorber using TEA. Solubility data for H_2S and CO_2 individually in TEA solutions were obtained in this laboratory (Jou et al., 1985). The present work was undertaken to provide information on the effect of mixtures of the acid gases on their solubility in triethanolamine solutions.

Experimental Section

Amine solutions were prepared from distilled water and triethanolamine having a purity of 99.4% obtained from Fisher Scientific. Hydrogen sulfide and carbon dioxide were obtained from Matheson and Linde, respectively, and had purities greater than 99%. The equipment used to determine the solubility data was that previously used in our laboratory (Jou et al., 1985). The apparatus consisted of a Jerguson liquid level gauge with a 50 cm^3 tubular gas reservoir mounted on the top. A magnetically driven piston pump was used to circulate the gas phase and bubble it through the liquid solution. The total volume of the apparatus including the cell, gas reservoir, tubing, and the pump is 250 cm^3. The apparatus was mounted in an air bath of dimensions 0.61 × 0.91 × 1.22 m. The air bath was equipped with a 3000 W heater and a refrigeration unit and fan; it can be controlled to within ±0.5 °C. The temperature inside the cell was measured with an iron−constantan thermocouple with an accuracy of ±0.1 °C. The pressure in the cell was measured with two calibrated digital Heise gauges (0−10 MPa and 0−35 MPa). The Heise gauges have an accuracy of 0.1% of full scale according to a calibration against a dead-weight gauge. The TEA solution of the desired concentration was charged to the evacuated cell, and acid gases were then added in an amount determined by observation of the pressure. The vapor phase was analyzed with the gas chromatograph using a 3.65 m long, 6.35 mm o.d. column packed with Chromosorb 104, operated isothermally at 100 °C. To ensure that equilibrium was reached, the vapor was bubbled through the liquid for at least 8 h prior to sampling of the liquid phase. The liquid sample from the cell was passed into a 1.0 mol dm^{-3} NaOH solution to form involatile salts. The concentration of CO_2 in an aliquot of the liquid sample was determined by mixing the liquid with 0.1 mol dm^{-3} $BaCl_2$ solution to form a precipitate of $BaCO_3$. This precipitate was filtered off and washed. The $BaCO_3$ was titrated with 0.1 mol dm^{-3} HCl using methyl orange−xylene cyanol indicator. The concentration of H_2S in an aliquot of liquid sample was determined by mixing the

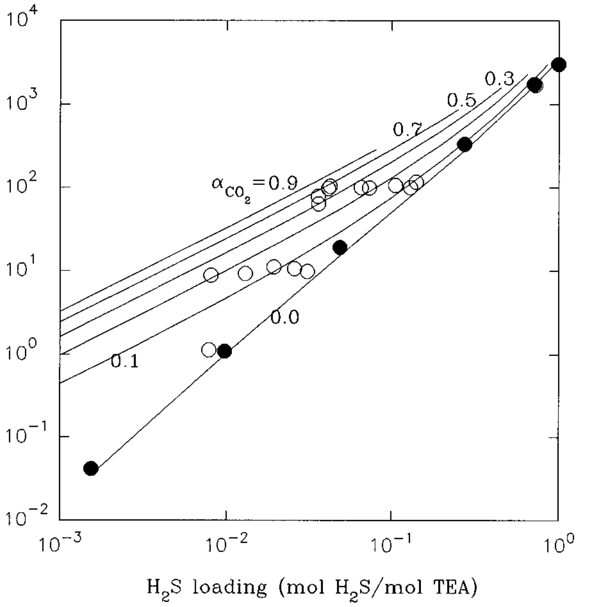

Figure 1. Effect of CO_2 on the solubility of H_2S in 3.5 mol dm^{-3} TEA solution at 100 °C: (●), H_2S; (○) H_2S + CO_2.

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Table 1. Solubility of H_2S + CO_2 Mixtures in 2.0 mol dm^{-3} TEA Solution

total pressure	partial pressures		mole ratio in liquid (mol/mol)	
P/kPa	p_{H_2S}/kPa	p_{CO_2}/kPa	H_2S/TEA	CO_2/TEA
50 °C				
1750	1050.0	447.0	1.017	0.239
728	465.0	180.0	0.765	0.196
596	32.7	232.0	0.109	0.609
1840	25.9	1800.0	0.0263	1.079
3630	15.7	3600.0	0.0115	1.332
200	4.74	72.8	0.0336	0.321
200	1.47	5.21	0.0373	0.0703
5670	1.07	5650.0	0.00119	1.378
200	0.678	0.401	0.0388	0.0117
424	0.530	1.42	0.0242	0.0317
478	11.4	3.97	0.159	0.0343
478	63.7	4.55	0.404	0.0202
501	75.8	38.5	0.391	0.149
488	296.0	55.5	0.733	0.0974
502	82.7	86.4	0.343	0.272
75 °C				
3680	1610.0	2020.0	0.810	0.454
860	547.0	273.0	0.658	0.132
600	535.0	26.5	0.727	0.0163
1500	274.0	1180.0	0.269	0.512
519	93.2	94.0	0.254	0.116
453	47.2	113.0	0.152	0.154
562	38.6	37.9	0.167	0.0806
506	23.2	102.0	0.0913	0.181
485	18.0	44.6	0.0943	0.0959
495	13.1	9.31	0.0963	0.0315
537	32.2	103.0	0.121	0.157
464	23.1	2.38	0.141	0.00909
3610	17.8	3550	0.013	1.038
729	13.8	269.0	0.0416	0.357
524	13.0	457.0	0.0261	0.450
5790	5.97	5740.0	0.00438	1.170
542	4.40	9.46	0.0477	0.0402
465	0.0283	0.287	0.00206	0.0060
100 °C				
4000	1330.0	2560.0	0.648	0.526
6090	1210.0	4770.0	0.466	0.714
1730	1040.0	569.0	0.703	0.175
2820	550.0	2170.0	0.343	0.553
686	175.0	418.0	0.225	0.215
532	114.0	5.88	0.221	0.00267
612	75.2	188.0	0.134	0.0869
480	65.1	13.0	0.155	0.00826
449	38.8	3.04	0.113	0.00255
558	9.43	22.3	0.0447	0.0285
508	2.67	1.85	0.0249	0.00434
592	0.623	2.10	0.0102	0.00766
508	0.224	0.637	0.00523	0.00413
507	60.8	354.0	0.105	0.214
1110	14.2	935.0	0.020	0.386
473	7.44	82.2	0.0252	0.0949
521	6.25	40.4	0.0282	0.0650

liquid with an excess of acidic 0.1 mol dm^{-3} iodine solution. The excess iodine was back-titrated with 0.1 mol dm^{-3} $Na_2S_2O_3$ solution using starch indicator. The concentration of TEA in the solution was determined by titration of an aliquot of liquid sample with 1.0 mol dm^{-3} H_2SO_4 solution using methyl red indicator. Replicate measurements indicated that the uncertainty in the solubility is less than 5%.

Results and Discussion

The solubility of mixtures of hydrogen sulfide and carbon dioxide in (2.0, 3.5, and 5.0) mol dm^{-3} triethanolamine solutions has been measured at (50, 75, and 100) °C at partial pressures of the acid gases up to 5490 kPa. The results are presented in Tables 1−3.

Table 2. Solubility of H_2S + CO_2 Mixtures in 3.5 mol dm^{-3} TEA Solution

total pressure	partial pressures		mole ratio in liquid (Mol/Mol)	
P/kPa	p_{H_2S}/kPa	p_{CO_2}/kPa	H_2S/TEA	CO_2/TEA
50 °C				
3050	325.0	2710.0	0.179	0.985
935	108.0	816.0	0.141	0.714
533	104.0	34.2	0.375	0.0737
510	98.6	3.08	0.392	0.00654
2960	32.2	2910.0	0.0208	1.038
452	17.4	93.7	0.0844	0.258
517	11.1	130.0	0.0483	0.330
569	10.3	548.0	0.0206	0.683
510	9.74	13.2	0.0906	0.0751
531	8.22	36.0	0.0627	0.164
2750	2.71	2730.0	0.00288	1.1156
495	0.400	0.381	0.0167	0.00716
75 °C				
513	10.2	1.50	0.0584	0.00299
479	9.97	17.0	0.0471	0.0271
493	11.0	160.0	0.0302	0.160
717	7.40	677.0	0.0128	0.392
2970	12.5	2920.0	0.00911	0.745
513	120.0	9.98	0.240	0.00679
572	101.0	77.7	0.207	0.0666
384	100.0	238.0	0.169	0.156
936	104.0	798.0	0.122	0.380
2860	77.8	2747.0	0.0519	0.713
589	330.0	221.0	0.420	0.123
2030	1630.0	165.0	0.955	0.0446
1510	681.0	784.0	0.513	0.255
451	5.10	20.8	0.0277	0.0362
541	2.97	0.879	0.0282	0.0024
100 °C				
1130	995.0	49.8	0.529	0.0061
1820	993.0	737.0	0.494	0.130
529	99.7	7.96	0.135	0.00303
1980	1410.0	483.0	0.632	0.0534
2950	1060.0	1800.0	0.459	0.237
514	9.76	6.79	0.0308	0.00526
483	10.5	45.4	0.0258	0.0297
676	11.0	187.0	0.0193	0.0964
476	9.15	382.0	0.0130	0.152
1700	8.83	1600	0.00808	0.341
1850	1700	63.0	0.724	0.00690
3310	63.8	3160	0.0359	0.517
138	1.13	3.30	0.0078	0.00495
573	100	67.8	0.129	0.0241
600	105	410	0.105	0.115
479	116	48.9	0.140	0.0164
2140	100	1960	0.065	0.386
1470	98.9	1290	0.073	0.278
4460	78.1	4300	0.0358	0.605
5680	97.8	5490	0.0414	0.639
5670	103	5480	0.0422	0.666
4390	8.62	4290	0.00451	0.598
2550	1520	939	0.634	0.127
1820	1020	716	0.495	0.108
5730	907	4730	0.298	0.458
4200	992	3120	0.371	0.350
5290	4260	945	0.0767	0.222
6180	3830	2270	0.192	0.995
2850	1790	976	0.705	0.108
2320	1270	964	0.577	0.149
558	1.74	109	0.0410	0.0665
521	18.7	92.1	0.397	0.0518
528	171	114	0.164	0.0323
1190	1020	105	0.534	0.0155

In mixtures of H_2S and CO_2, the acid gases compete for the available base in the solution. Hence the solubility of one acid gas is decreased by the presence of the other acid gas. The effect can be seen in Table 4 in which selected values from Table 2 at partial pressures of H_2S near 10 and 100 kPa show clearly the decrease in solubility of H_2S with increasing concentration of CO_2 in the liquid phase.

Table 3. Solubility of $H_2S + CO_2$ Mixtures in 5.0 mol dm^{-3} TEA Solution

total pressure	partial pressures		mole ratio in liquid (Mol/Mol)	
P/kPa	p_{H_2S}/kPa	p_{CO_2}/kPa	H_2S/TEA	CO_2/TEA
		50 °C		
506	10.0	14.3	0.0440	0.0325
541	10.3	75.6	0.0389	0.128
2320	10.2	2290.0	0.0088	0.804
512	99.2	36.2	0.274	0.0501
594	101.0	158.0	0.228	0.170
600	99.8	492.0	0.159	0.341
2630	98.6	2520.0	0.0674	0.804
		75 °C		
403	0.379	0.134	0.00523	0.000445
437	5.01	1.02	0.0208	0.00103
444	7.02	32.2	0.0199	0.0240
548	2.64	7.44	0.0123	0.00838
550	4.81	89.4	0.0122	0.0549
680	6.37	237	0.0115	0.101
687	7.05	614	0.0085	0.181
950	235.0	652	0.189	0.177
2170	254.0	1870	0.151	0.357
782	119.0	633	0.113	0.157
577	73.6	284	0.0933	0.119
515	3.59	29.4	0.0133	0.0262
496	10.1	29.4	0.0277	0.0223
501	10.3	109.0	0.0215	0.0608
534	7.52	493.0	0.010	0.184
2100	9.14	2060.0	0.00809	0.464
2210	103.0	2080.0	0.0674	0.422
641	101.0	20.2	0.152	0.00938
536	92.9	257.0	0.113	0.0995
		100 °C		
530	12.7	3.25	0.0217	0.00111
512	127.0	31.0	0.0861	0.00546
496	8.08	5.51	0.0143	0.00209
455	21.3	21.6	0.0271	0.00558
485	73.5	13.1	0.0651	0.00286
377	218	82.0	0.133	0.0122
794	384	263	0.226	0.0387
2040	618	692	0.259	0.0772
1080	13.9	575	0.00738	0.0785
516	11.7	110	0.0133	0.0255
674	7.83	83.9	0.0110	0.0260
674	5.49	10.0	0.0118	0.00404

Table 4. Effect of CO_2 on the Solubility of H_2S in 3.5 mol dm^{-3} TEA Solution at 100 °C

p_{H_2S}/kPa	α_{H_2S}/(mol of H_2S/ mol of TEA)	α_{CO_2}/(mol of CO_2/ mol of TEA)
9.76	0.0308	0.00526
10.5	0.0258	0.0297
11.0	0.0193	0.0964
9.15	0.0130	0.152
8.83	0.00808	0.341
99.7	0.135	0.00303
100	0.129	0.0241
105	0.105	0.115
98.9	0.073	0.278
100	0.065	0.386
97.8	0.0414	0.639
103	0.0422	0.666
78.1	0.0358	0.605
63.8	0.0359	0.517

Here the liquid concentrations are given as α_{H_2S} and α_{CO_2}, moles of acid gas/moles of TEA. The abridged results are presented in Figure 1, where the points labeled H_2S only were taken from Jou et al. (1985). The effect is similar at other concentrations and temperatures.

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