Solubility of Hydrogen Sulfide in Aqueous Diethanolamine Solutions at High Pressures

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The solubility of hydrogen sulfide in aqueous solutions of diethanolamine has been determined at temperatures between 25° and 120°C in two solutions, 2*N* and 3.5*N* DEA. The partial pressures of H_2S ranged from 0.1 psia to 306 psia. Enthalpies of solution have been calculated from the experimental results.

Few investigations of the solubility of hydrogen sulfide in aqueous diethanolamine (DEA) solutions have been made. Bottoms *(2)* presented a small-scale plot showing the solubility of H_2S in 50% water solution at temperatures of 25°, 35°, 45°, and 55°C, and partial pressures of H_2S up to 760 mm Hg. A note in the paper of Riegger et al. *(6)* indicated that J. W. Mason determined the equilibrium for hydrogen sulfide and diethanolamine solutions, but this work was not published. Leibush and Shneerson *(5)* studied the solubility of H_2S in 0.97*N* and 2.0*N* solutions at temperatures of 15°, 25°, and 50°C, and partial pressures of H_2S ranging from 0.0048 to 219 mm Hg. Atwood et al. *(1)* present a few values for the solubility of H_2S in solutions containing 10, 25, and 50 wt % DEA at temperatures between 80° and 140°F and partial pressures of H_2S below 712 mm Hg. The published results have been summarized by Kohl and Riesenfeld *(3)*. The purpose of the present work is to provide data on the solubility of H_2S in DEA solutions at partial pressures above 1 atm over the range of temperatures and solution concentrations used industrially for the removal of the acid gases, H_2S and CO_2, from gaseous mixtures.

Experimental

The amine solutions were prepared from distilled water and commercially available DEA, which had a purity of 99.8%. Nitrogen and hydrogen sulfide were also obtained from commercial suppliers. The hydrogen sulfide was C.P. grade. It was cooled to the ice point and the vapor phase removed several times. The vapor from the cylinder after this operation was 99.91 mol % H_2S, 0.07 mol % CO_2, and 0.02 mol % N_2.

The experimental apparatus and procedure differ somewhat from that used in the previous work with CO_2 *(4)*. The equilibrium cell used here consisted of a Jerguson liquid level gage (Model 19-T-20) with a 250-cm^3 tubular gas reservoir mounted at the top. A magnetic pump *(7)* was used to circulate the gas phase from the reservoir to the bottom of the Jerguson gage. This resulted in equilibrium being reached in a much shorter time. The temperature of the cell was measured by duplicate 10-junction copper-constantan thermopiles which had been calibrated at the ice point and the steam point. The cell was housed in an air bath controlled within ±0.5°C. The pressure in the cell was measured by a calibrated Heise bourdon tube gage. The chromatograph used for analyses had a 10 ft long, ¼ in. o.d. column packed with Chromosorb 104 and was operated isothermally at 130°C.

The DEA solution was made up to the desired strength and about 150 cm^3 were charged to the cell which had been purged with nitrogen. Hydrogen sulfide was then added to an amount determined by observation of the pressure. Nitrogen was added to increase the total pressure and to ensure that it was always superatmospheric. At partial pressures of H_2S above 50 psia, no nitrogen was added so that the vapor phase was almost entirely H_2S. The circulation pump was started and the vapor bubbled through the liquid for at least 3 hr. The circulation was stopped and vapor was withdrawn from the top of the cell and passed to the chromatograph for analysis. The partial pressures of the acid gases were obtained by multiplying the difference between the system pressure and the vapor pressure of the amine solution by the mole fractions of the dry acid gases. Liquid samples were withdrawn from the bottom of the cell and passed into a weighed amount of 5*N* H_2SO_4 contained in a sample bottle closed with a rubber septum. On contact with the sulfuric acid, the acid gases evolved and were collected in a calibrated buret of 200 cm^3 capacity. The pressure of the evolved gases was adjusted to atmospheric and their temperature was measured. From the *P-V-T* data the amount of gas which evolved was calculated. Samples of this gas were then passed to the chromatograph for determination of its composition. Analyses of the acidic solution did not show sulfur, indicating that the hydrogen

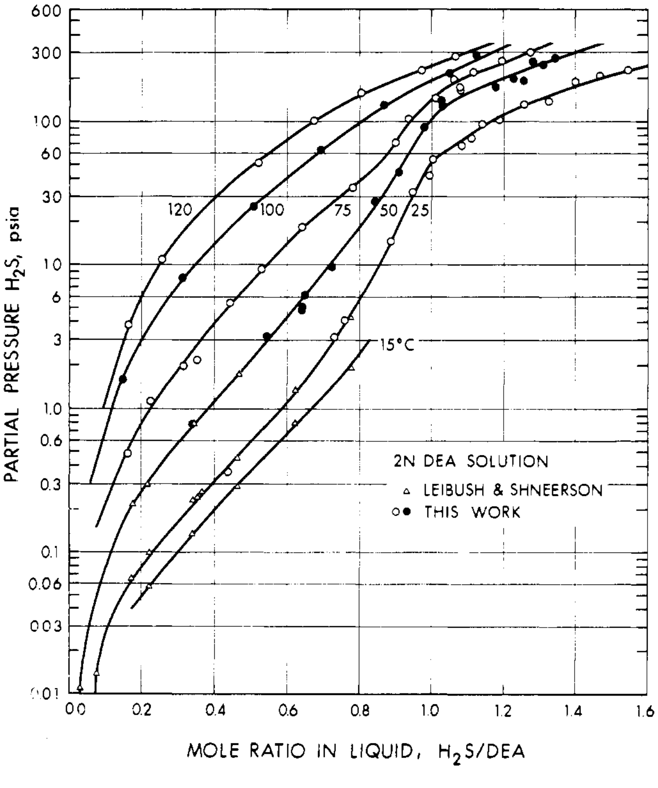

Figure 1. Solubility of hydrogen sulfide in 2*N* diethanolamine solution

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Table I. Solubility of H_2S in 2*N* DEA Solution
(α, mole ratio in the liquid phase, acid gas/DEA)

	p, psia			α		
Temp, °C	H_2S	CO_2	Total	H_2S/ DEA	CO_2/ DEA	Total
25	0.356	0.00	0.356	0.440	0.003	0.443
	3.20	0.00	3.20	0.731	0.003	0.734
	3.99	Trace	3.99	0.761	0.004	0.765
	14.48	0.01	14.49	0.888	0.003	0.891
	32.20	0.02	32.22	0.944	0.001	0.945
	40.90	0.19	41.09	0.994	0.008	1.002
	52.64	0.10	52.74	1.005	0.003	1.008
	66.65	0.55	67.20	1.087	0.002	1.089
	74.90	0.07	74.97	1.111	0.001	1.112
	94.50	0.12	94.62	1.140	0.002	1.142
	102.0	0.14	102.1	1.188	0.002	1.190
	130.5	0.19	130.7	1.256	0.002	1.258
	136.0	0.12	136.1	1.326	0.002	1.328
	183.8	1.32	185.1	1.398	0.010	1.408
	206.2	0.32	206.5	1.467	0.001	1.468
	221.2	0.36	221.6	1.547	0.002	1.549
50	0.785	0.00	0.785	0.331	0.002	0.333
	3.17	0.00	3.17	0.542	0.003	0.545
	4.70	trace	4.70	0.635	0.009	0.644
	4.93	trace	4.93	0.641	0.002	0.643
	6.18	trace	6.18	0.646	0.005	0.651
	9.56	trace	9.56	0.724	0.002	0.726
	27.00	0.09	27.09	0.842	0.004	0.846
	43.60	0.08	43.68	0.910	0.002	0.912
	89.05	0.18	89.23	0.978	0.002	0.980
	131.0	0.51	131.5	1.028	0.004	1.032
	132.0	0.17	132.2	1.030	0.001	1.031
	145.2	0.98	146.2	1.023	0.005	1.028
	165.1	0.22	165.3	1.180	0.001	1.181
	193.3	0.59	193.9	1.255	0.003	1.258
	199.2	0.24	199.4	1.227	0.001	1.228
	240.1	0.78	240.9	1.310	0.003	1.313
	250.7	1.66	252.4	1.275	0.006	1.281
	274.5	0.32	274.8	1.347	0.001	1.348
75	0.472	0.00	0.472	0.159	0.002	0.161
	1.12	0.00	1.12	0.226	0.002	0.228
	1.95	trace	1.95	0.316	0.002	0.318
	2.19	0.00	2.19	0.354	0.001	0.355
	5.40	trace	5.40	0.445	0.002	0.447
	9.14	trace	9.14	0.530	0.001	0.531
	18.58	0.02	18.60	0.639	0.002	0.641
	33.20	0.02	33.22	0.783	0.001	0.784
	69.10	0.10	69.20	0.905	0.001	0.906
	103.0	0.20	103.2	0.938	0.001	0.939
	141.3	0.22	141.5	1.012	0.001	1.013
	165.3	0.22	165.5	1.079	0.001	1.080
	167.1	0.22	167.3	1.080	0.001	1.081
	198.0	0.42	198.4	1.062	0.001	1.063
	214.0	0.28	214.3	1.117	0.001	1.118
	258.0	0.47	258.5	1.200	0.001	1.201
	290.1	0.43	290.5	1.274	0.001	1.275
100	1.60	trace	1.60	0.150	0.002	0.152
	8.36	0.02	8.38	0.314	0.001	0.315
	25.60	0.06	25.66	0.506	0.002	0.508
	62.25	0.13	62.38	0.694	0.001	0.695
	129.0	0.23	129.2	0.873	0.002	0.875
	208.1	0.29	208.4	1.053	0.001	1.054
	275.0	0.22	275.2	1.127	0.001	1.128
	285.5	0.45	286.0	1.131	0.001	1.132
120	3.66	0.10	3.76	0.162	0.003	0.165
	10.80	0.10	10.90	0.256	0.002	0.258
	49.60	0.19	49.79	0.521	0.001	0.522
	99.90	0.24	100.14	0.680	0.001	0.681
	151.2	0.26	151.4	0.812	0.001	0.813
	220.0	0.32	220.3	0.975	0.001	0.976
	278.0	0.37	278.4	1.062	0.001	1.063
	279.3	0.29	279.6	1.070	0.001	1.071

sulfide was not oxidized by the acid. The sample bottle was reweighed to determine the quantity of amine solution from which the gases evolved. From these results the ratios of H_2S and CO_2 to amine in the liquid phase were calculated.

Results and Discussion

As a check on the analytical technique, the solubility of H_2S in water was determined at 50°C at partial pressures of H_2S between 80 and 250 psia. These results agreed with interpolated values from the literature *(8)* within a few percent.

Experimental data for the solubility of H_2S in 2.0 and 3.5*N* DEA solutions were obtained at temperatures of 25°, 50°, 75°, 100°, and 120°C at partial pressures of H_2S ranging from 0.1 to 306 psia. The results are presented in Tables I and II and are shown in Figure 1. Figure 1 shows that the present work is in good agreement with the results of Leibush and Shneerson *(5)*.

The major sources of error in this work are associated with the determination of the partial pressure of the acid gases and the measurement of the pressure, volume, and composition of the gases evolved from the liquid sample. Other errors result from uncertainties in the temperature of the equilibrium cell and the gas buret, error in the determination of the normality of the solutions, and errors in weighing in determination of the amine in the liquid sample. The data presented here are estimated to be accurate within 3–5% in liquid concentration at a given partial pressure of hydrogen sulfide.

Approximate values of the enthalpy of solution of H_2S in the amine solutions were calculated from the equation

$$\Delta H_S/R = (H_1^* - \bar{H}_1^l)/R = [\partial \ln p_1/\partial(1/T)]_{x_1}$$

where the subscript 1 refers to H_2S. The plots of $\ln p_1$ vs. $1/T$ were linear within the accuracy of the data, indicating that ΔH_S is independent of temperature over the range of temperatures of this work. The values of ΔH_S are presented in Table III. The enthalpy of solution depends strongly on the loading of H_2S in solution; for the two solutions studied here it is not possible to decide whether it is a function of the normality of the solution. Kohl and Riesenfeld *(3)* give a value of 511 Btu/lb_m of H_2S for the enthalpy of solution of H_2S in DEA solutions. This corresponds to 40.5 kJ/mol of H_2S, in agreement with the present results at moderate loadings of H_2S in the DEA solutions.

Nomenclature

α = mole ratio, acid gas/DEA
H = enthalpy, J mol^{-1}
p = partial pressure, y_1P, psia

Table II. Solubility of H_2S in 3.5*N* DEA Solution
(α, mole ratio in the liquid phase, acid gas/DEA)

Temp, °C	*p*, psia			α		
	H_2S	CO_2	Total	H_2S/DEA	CO_2/DEA	Total
25	0.121	Trace	0.121	0.201	0.003	0.204
	0.565	Trace	0.565	0.352	0.002	0.354
	0.981	Trace	0.981	0.449	0.001	0.450
	2.45	Trace	2.45	0.613	0.002	0.615
	5.20	Trace	5.20	0.681	0.001	0.682
	7.03	Trace	7.03	0.711	0.002	0.713
	14.50	0.00	14.50	0.785	0.000	0.785
	16.10	0.00	16.10	0.790	0.000	0.790
	38.60	0.00	38.60	0.875	0.000	0.875
	56.52	0.00	56.52	0.948	0.000	0.948
	106.3	0.04	106.3	1.020	0.001	1.021
	150.4	0.05	150.5	1.103	0.001	1.104
	196.9	0.07	197.0	1.120	0.001	1.121
	254.7	0.07	255.4	1.206	0.001	1.207
50	0.107	Trace	0.107	0.064	0.003	0.067
	0.735	Trace	0.735	0.200	0.003	0.203
	3.16	Trace	3.16	0.387	0.002	0.389
	9.69	Trace	9.69	0.616	0.002	0.618
	17.90	Trace	17.90	0.713	0.001	0.713
	31.90	Trace	31.90	0.776	0.000	0.776
	56.90	Trace	56.90	0.858	0.000	0.858
	97.50	0.04	97.54	0.918	0.000	0.918
	135.7	0.06	135.8	0.975	0.000	0.975
	201.0	0.11	201.1	1.039	0.000	1.039
	288.0	0.18	288.2	1.097	0.001	1.098
75	0.342	Trace	0.342	0.072	0.002	0.074
75	1.78	0.02	1.80	0.198	0.003	0.201
	8.62	0.03	8.65	0.396	0.002	0.398
	24.2	0.05	24.3	0.614	0.002	0.616
	44.6	0.03	44.6	0.723	0.000	0.723
	85.5	0.06	85.6	0.831	0.000	0.831
	126.4	0.10	126.5	0.855	0.000	0.855
	209.0	0.18	209.2	0.945	0.000	0.945
	305.3	0.16	305.5	1.042	0.001	1.043
100	0.793	0.098	0.891	0.069	0.002	0.071
	4.92	0.06	4.98	0.193	0.003	0.196
	20.2	0.09	20.3	0.391	0.002	0.393
	32.8	0.11	32.9	0.478	0.002	0.480
	51.8	0.09	51.9	0.582	0.001	0.583
	74.3	0.04	74.3	0.675	0.000	0.675
	87.2	0.13	87.3	0.688	0.001	0.689
	133.6	0.17	133.8	0.762	0.001	0.763
	197.6	0.25	197.9	0.830	0.000	0.830
	301.1	0.11	301.2	0.927	0.000	0.927
120	1.93	0.07	2.00	0.069	0.002	0.071
	11.35	0.22	11.57	0.187	0.003	0.190
	36.7	0.23	36.9	0.365	0.001	0.366
	52.4	0.55	53.0	0.440	0.001	0.441
	98.3	0.13	98.4	0.618	0.000	0.618
	108.8	0.22	109.0	0.625	0.001	0.626
	179.6	0.20	179.8	0.725	0.000	0.725
	290.6	0.21	290.8	0.836	0.000	0.836

Table III. Enthalpy of Solution of H_2S in DEA Solutions

α Mole ratio in liquid H_2S/DEA	$-\Delta\bar{H}_S$, kJ/g-mol H_2S
0.2	47.7
0.4	43.5
0.6	40.0
0.8	31.9
1.0	16.4
1.2	12.5
1.4	11.0

P = total pressure, psia
R = gas constant
T = temperature, °C
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Subscripts

1 = H_2S
S = solution

Superscripts

‾ = partial molar quantity
* = ideal gas state
l = liquid

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Received for review July 17, 1972. Accepted October 20, 1972. The authors are grateful to the National Research Council of Canada for financial support.