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Solubility of Mixtures of H_2S and CO_2 in a Monoethanolamine Solution at Low Partial Pressures

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The solubility of H_2S, CO_2, and their mixtures in a 2.5 kmol m^{-3} aqueous solution of monoethanolamine has been determined at 100 °C at partial pressures of acid gases between 0.003 and 3.36 kPa. The results for the mixture have been compared with values calculated by two methods of prediction.

Aqueous monoethanolamine solutions are used extensively for the removal of the acid gases (H_2S and CO_2) from gas streams. Advantages of the use of monoethanolamine (MEA) solutions include their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (*2*). Most of the data on the equilibrium solubility of the acid gases in MEA solutions is in the range of partial pressures from 1 to 5000 kPa. There is a need for data at conditions typical of the operation of amine regenerators and at the top of amine contactors. In this laboratory, data have recently been obtained at these conditions (*9*). The present work was undertaken, after modifications of the low-pressure apparatus, to extend the measurements of solubility to a less-concentrated MEA solution.

Experimental Section

The apparatus used by Nasir and Mather (*9*) has been modified and the present apparatus is shown schematically in Figure 1. It was designed to allow operation over a wide range of temperatures and pressures. It consisted of three double-ended stainless steel cylinders (each 500 cm^3 capacity) with a welded side arm, connected in series. The assembly was immersed in an oil bath controlled within ±0.5 °C; the bath temperature was measured by a calibrated iron–Constantan thermocouple. Carrier nitrogen gas was saturated with water vapor and passed through a 9 m long, 6.35 mm o.d. stainless steel coil immersed in the oil bath. The nitrogen then bubbled through the three cylinders and the flow of nitrogen was regulated by a low-pressure line regulator at the inlet. A relatively constant back-pressure was maintained by the use of a pneumatically controlled valve utilizing a differential pressure transmitter. Each of the cylinders contained 250–400 mL of solution with a certain concentration of CO_2 and/or H_2S. Stainless steel filter elements welded to the ends of the dip tubes were used to disperse the gas into the solution in the cylinders. After passing through the three cylinders, the gas stream passed through a trap to remove condensed liquid before entering a chromatograph, a soap bubble flow meter, and the exhaust. A mercury manometer was used to measure the gauge pressure in the last cylinder.

Two aqueous MEA stock solutions, one saturated with CO_2 and the other with H_2S at atmospheric pressure, were prepared in a well-ventilated hood. Aliquots of these solutions were used to prepare a solution of the desired concentration of CO_2 and/or H_2S. This solution was charged to the cylinders individually by applying N_2 pressure above the solution in a filling bottle and forcing the liquid into the tubing leading to the bottom of each cylinder. Liquid samples for analysis were withdrawn from the last cylinder by applying back-pressure to force solution up through the filter element and out to the liquid sampling valve (*12*).

Table I. Experimental Data for the Solubility of CO_2 in 2.5 kmol m^{-3} MEA Solution[a]

T/°C	p	α
80	0.00896	0.0368
	0.0124	0.0395
	0.0193	0.0436
	0.116	0.121
	0.331	0.185
	0.393	0.200
	0.397	0.206
	0.558	0.223
	0.731	0.266
	1.10	0.287
	1.75	0.315
100	0.0066	0.0350
	0.0220	0.0470
	0.0180	0.0500
	0.186	0.106
	1.04	0.164
	0.973	0.165
	1.38	0.178
	1.64	0.194

[a] α, mole ratio in liquid, CO_2/MEA. p, partial pressure of CO_2 in kPa.

The time required to reach equilibrium was dependent on the concentration of the acid gases in the liquid and the flow rate of the nitrogen gas. Rapid flow rates have the advantage of allowing equilibrium to be reached sooner; however, too rapid a flow rate results in excessive removal of water and hence an appreciable change in amine concentration. The range of nitrogen gas flow rates used was 3–6 mL min^{-1}. Once equilibrium had been attained, the gauge and barometric pressures were measured and a liquid sample was taken. From the pressure readings and the gas-phase analysis, the partial pressure of the acid gas(es) was calculated. The liquid sample was analyzed to determine α_{CO_2}, α_{H_2S}, and the amine concentration.

A Model 5710A Hewlett-Packard gas chromatograph equipped with a Model 3380A reporting integrator was used for the gas analysis. The column was a 3.65 m × 6.35 mm o.d. tube packed with Chromosorb-104 and was operated isothermally at 100 °C. The CO_2 in an aliquot of the liquid sample was precipitated as $BaCO_3$ in the presence of excess $BaCl_2$. The solution was filtered and the $BaCO_3$ titrated with 0.1 N HCl using modified methyl orange indicator. The H_2S in an aliquot of the liquid sample was determined by using the iodine–thiosulfate titration with starch as an indicator. The method has been outlined by Vogel (*10*) and Belcher and Nutten (*1*). The amine concentration was determined by direct titration of an aliquot of the liquid sample with H_2SO_4 solution using methyl red indicator.

Results

To test the apparatus and to confirm the sampling and analytical procedures, we obtained data at conditions at which data had previously been reported in the literature. Measurements were made for CO_2 at 80 and 100 °C, and a few determinations for H_2S at 100 °C were made in a 2.5 kmol m^{-3} MEA solution. The results are presented in Table I and II for the CO_2 and H_2S

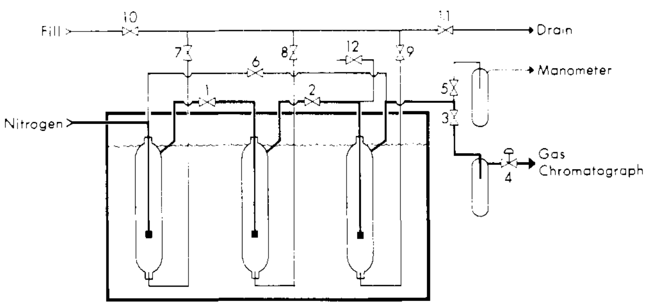

Figure 1. Schematic diagram of the experimental apparatus.

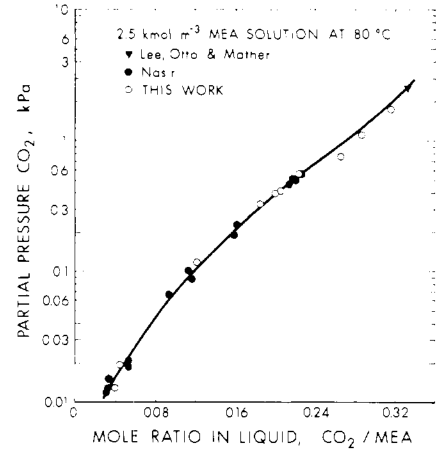

Figure 2. Solubility of CO_2 in 2.5 kmol m^{-3} MEA solution at 80 °C.

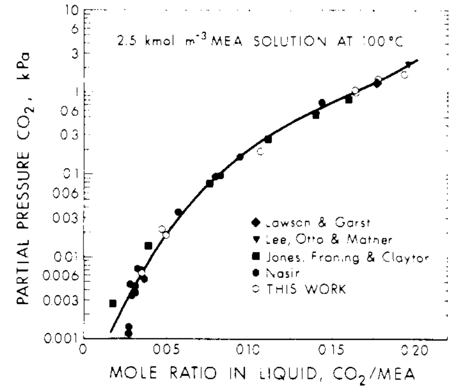

Figure 3. Solubility of CO_2 in 2.5 kmol m^{-3} MEA solution at 100 °C.

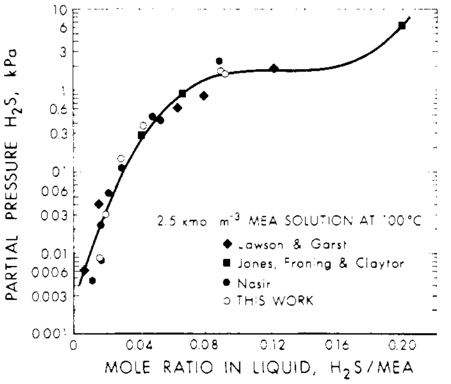

Figure 4. Solubility of H_2S in 2.5 kmol m^{-3} MEA solution at 100 °C.

solutions, respectively. Figures 2–4 compare the results for the individual acid gases at 80 and 100 °C with data previously published. The solid line in these figures is the result of a least-squares fit of all data to a polynomial of the form

$$\ln p_i = a_0 + a_1\alpha_i + a_2\alpha_i^2 + a_3\alpha_i^3$$

Table II. Experimental Data for the Solubility of H_2S in 2.5 kmol m^{-3} MEA Solution at 100 °C[a]

p	α	p	α
0.0090	0.016	0.354	0.0430
0.0310	0.0210	1.67	0.090
0.140	0.0300	1.50	0.092

[a] α, mole ratio in liquid, H_2S/MEA. p, partial pressure of H_2S in kPa.

Table III. Experimental Data for the Solubility of H_2S-CO_2 Mixtures in 2.5 kmol m^{-3} MEA Solution at 100 °C[a]

p/kPa		α	
H_2S	CO_2	H_2S/MEA	CO_2/MEA
trace	0.886	trace	0.149
trace	0.0337	0.0067	0.0600
0.0353	0.00714	0.0181	0.0182
0.0590	0.0198	0.0187	0.0357
0.0842	0.0297	0.0205	0.0310
0.0601	0.0140	0.0213	0.0217
0.0242	0.0408	0.0219	0.0347
0.138	0.0490	0.0231	0.0312
0.149	0.0453	0.0232	0.0295
0.120	0.0331	0.0238	0.0261
0.121	0.0242	0.0239	0.0197
0.102	0.0214	0.0247	0.0227
0.140	0.0163	0.0248	0.0210
0.211	0.0511	0.0263	0.0297
0.499	0.565	0.0265	0.108
0.237	0.0834	0.0269	0.0467
0.138	0.0270	0.0272	0.0213
0.133	0.0222	0.0277	0.0211
0.131	0.0067	0.0325	0.0100
0.314	0.0568	0.0326	0.0310
0.583	0.244	0.0338	0.0791
0.432	0.155	0.0340	0.0492
0.544	0.246	0.0365	0.0718
0.329	0.0714	0.0369	0.0375
0.424	0.0906	0.0382	0.0357
0.260	0.0780	0.0388	0.0406
0.476	0.0962	0.0400	0.0400
0.548	0.140	0.0400	0.0492
0.620	0.137	0.0409	0.0485
0.458	0.0545	0.0418	0.0254
0.561	0.126	0.0420	0.0462
0.778	0.135	0.0425	0.0457
0.391	0.0048	0.0459	0.0085
0.823	0.220	0.0504	0.0593
0.752	0.211	0.0507	0.0610
0.949	0.242	0.0518	0.0711
0.928	0.206	0.0536	0.0606
0.851	0.204	0.0537	0.0516
1.28	0.438	0.0555	0.0851
0.932	0.248	0.0567	0.0545
1.18	0.239	0.0570	0.0686
0.966	0.116	0.0612	0.0332
1.84	0.523	0.0654	0.0941
1.24	0.132	0.0735	0.0333
2.56	0.838	0.0748	0.115
1.21	0.0027	0.0755	0.0062
1.63	0.164	0.0846	0.0327
2.10	0.195	0.0872	0.0401
2.03	0.169	0.0924	0.0363
3.92	1.36	0.0954	0.141
2.81	0.355	0.122	0.0407
3.36	0.0800	0.136	0.0062

[a] α, mol ratio in liquid, acid gas/MEA.

The results are seen to be in good agreement with the data of Jones et al. (*3*), Lawson and Garst (*6*), and data previously measured in this laboratory (*7*, *8*).

Data were obtained for mixtures of H_2S and CO_2 in a 2.5 kmol m^{-3} MEA solution at 100 °C at low loadings of the acid gases, and the results are presented in Table III Figures 5 and 6 show a comparison of the new data with a previous (*8*) extrapolation

Table IV. Comparison of the Present Work with Methods of Prediction 2.5 kmol m^{-3} Solution at 100 °C

		p_{H_2S}/kPa			p_{CO_2}/kPa		
	α_{H_2S}	this work	Klyamer	K & E	this work	Klyamer	K & E
$\alpha_{CO_2} = 0.00$	0.02	0.035	0.070	0.050			
	0.06	0.70	0.49	0.44			
	0.10	1.8	1.3	1.0			
$\alpha_{CO_2} = 0.02$	0.00				<0.001	0.024	0.009
	0.02	0.070	0.11	0.10	0.012	0.042	0.018
	0.06	0.83	0.64	0.62	0.052	0.082	0.038
	0.10	2.2	1.5	1.6	0.092	0.12	0.063
$\alpha_{CO_2} = 0.06$	0.00				0.042	0.20	0.09
	0.02	0.2	0.22	0.21	0.11	0.26	0.12
	0.06	1.1	0.96	1.0	0.25	0.40	0.20
	0.10	2.8	2.1	2.3	0.35	0.50	0.30
$\alpha_{CO_2} = 0.10$	0.00				0.19	0.60	0.30
	0.02	0.30	0.33	0.35	0.33	0.71	0.37
	0.06	1.7	1.3	1.5	0.58	0.96	0.55
	0.10	3.7	2.6	3.2	0.76	1.2	0.75

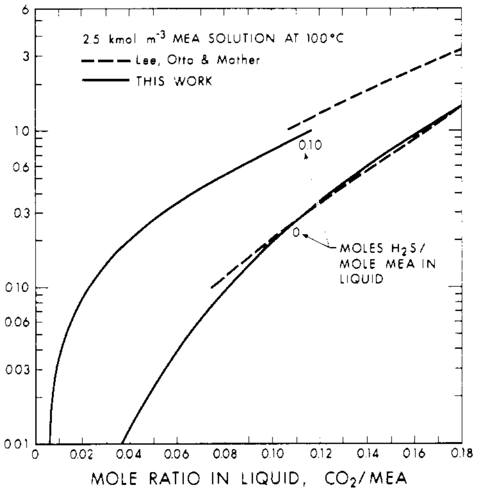

Figure 5. Effect of H_2S on the solubility of CO_2 in 2.5 kmol m^{-3} MEA solution at 100 °C.

of data which were obtained at higher pressures in a different apparatus. The agreement is generally better than ±15%; however, the new data do provide more accurate information about the equilibrium solubilities at low partial pressures.

Discussion

Klyamer et al. (*5*) and Kent and Eisenberg (*4*) have presented models that can be used to predict the partial pressures of acid gases over ethanolamine solutions. These models are described in detail in a previous paper (*8*). Predictions have been made, by using both models, for comparison with smoothed values at even liquid loadings obtained by plotting the data in Table III. The results are presented in Table IV. While neither method can be said to predict the experimental values with good accuracy, that of Kent and Eisenberg is consistently closer to experiment. Both methods postulate thermodynamic models for the reaction equilibria and use a number of equilibrium constants that must be determined independently. Kent and Eisenberg chose to partially avoid the uncertainty associated with the evaluation of equilibrium constants by obtaining two parameters from a best fit of experimental solubility data for CO_2 and H_2S dissolved individually in amine solutions. Thus, at this stage of development of the Klyamer model, one can expect the Kent and Eisenberg model to be in better agreement with experimental data. However the magnitude of deviations from experimental data obtained when using either model suggests that an improved correlation is desirable for the quantitative prediction of the partial pressure of the acid gases over monoethanolamine solutions.

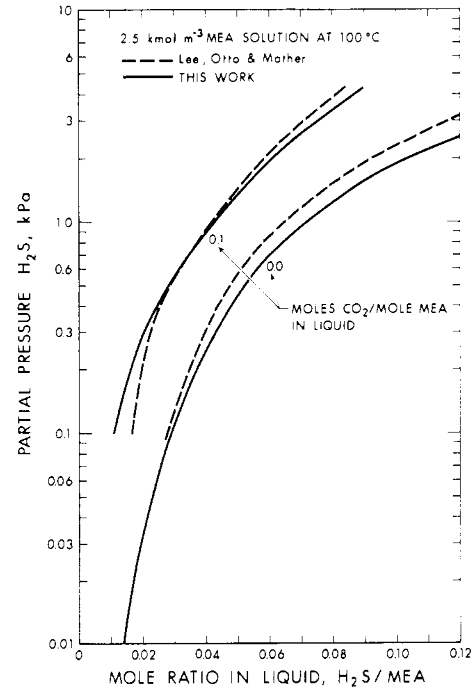

Figure 6. Effect of CO_2 on the solubility of H_2S in 2.5 kmol m^{-3} MEA solution at 100 °C.

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