R_{LL} = Lorentz-Lorenz molar refractivity
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
V_L = molar volume of liquid, ft^3/lb mol
V_V = molar volume of vapor, ft^3/lb mol
ρ = density

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Received for review June 6, 1974. Accepted November 14, 1974. Financial support provided by the Gas Processors Association.

Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 5.0*N* Monoethanolamine Solution

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The solubility of mixtures of carbon dioxide and hydrogen sulfide in 5.0*N* monoethanolamine solution was determined at temperatures of 40° and 100°C. Partial pressures of carbon dioxide ranged from about 0.1 to 810 psia and of hydrogen sulfide from 0.1 to 510 psia. The results were combined with data for the pure components, and smoothed values are presented.

Although a number of studies of the solubility of CO_2 and H_2S individually in aqueous monoethanolamine (MEA) solutions have been made, only a few workers have investigated the solubility of mixtures of CO_2 and H_2S in MEA solutions. All the studies of mixtures were made at partial pressures of the acid gases below 2 atm and for the 2.5*N* MEA solution. A literature review was made of the solubility of the individual acid gases in MEA solutions as part of a previous paper (*5*).

Three papers have been published on the solubility of mixtures of CO_2 and H_2S in MEA solutions. Leibush and Shneerson (*6*) measured the equilibrium solubilities for a 2.5*N* MEA solution at 25°C. Partial pressures of the acid gases were below 75 mm Hg. Muhlbauer and Monaghan (*7*) determined the solubility of mixtures of CO_2 and H_2S in a 2.5*N* MEA solution at 25° and 100°C, at partial pressures of the acid gases of less than 1000 mm Hg. Jones et al. (*1*) studied the solubility of mixtures of H_2S and CO_2 in a 2.5*N* MEA solution at temperatures between 60° and 120°C at partial pressures of CO_2 and H_2S up to 3000 and 1000 mm Hg, respectively.

Experimental

The MEA solution was made up to 5.0*N* from commercially available MEA and distilled water and charged to a windowed equilibrium cell. Carbon dioxide and hydrogen sulfide were added to amounts determined by observation of the total pressure on a bourdon gauge. The vapor phase was circulated by means of a magnetic pump and bubbled through the liquid. After equilibrium was reached, samples of the vapor and liquid were withdrawn for analysis. The apparatus and the analytical procedure have been described in previous papers (*2-4*).

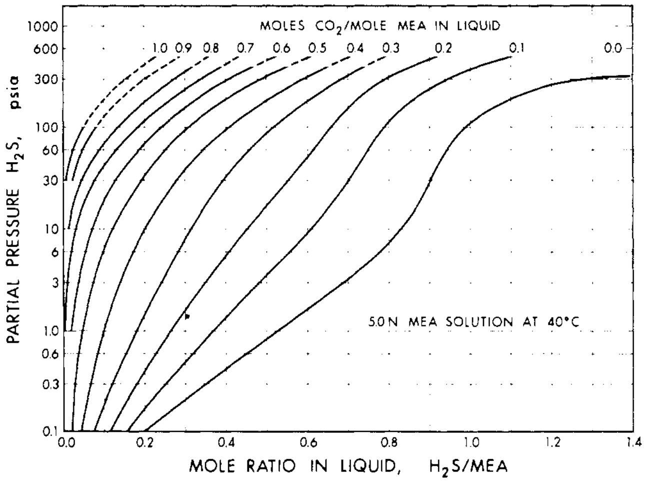

Figure 1. Effect of CO_2 on partial pressure of H_2S in 5.0*N* MEA solution at 40°C

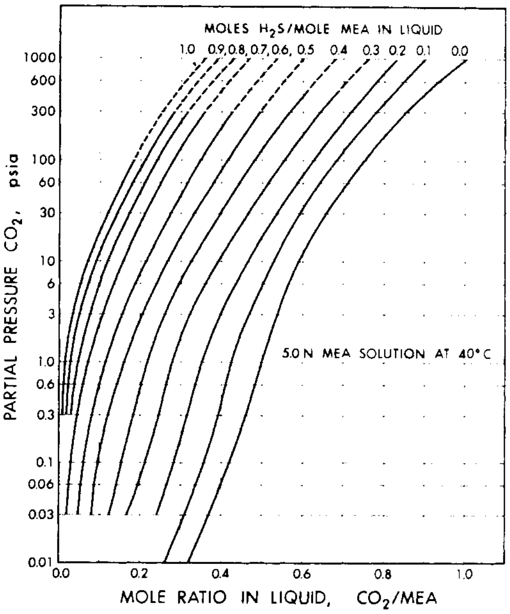

Figure 2. Effect of H_2S on partial pressure of CO_2 in 5.0*N* MEA solution at 40°C

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Table III. Smoothed Data for Solubility of Mixtures of Acid Gases in 5.0N Monoethanolamine Solution at 40°C

α, mole ratio in liquid, acid gas/MEA; p, partial pressure of acid gas, psia

	α_{CO_2}										
α_{H_2S}	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000
p_{CO_2}											
0.0100	0.316	0.258	...	...	...	...	...	...	...	...	...
0.0316	0.361	0.307	0.235	0.166	0.124	0.079	0.046	0.018	...	...	...
0.100	0.411	0.352	0.278	0.210	0.153	0.095	0.060	0.028	...	...	...
0.316	0.454	0.390	0.318	0.246	0.183	0.120	0.080	0.043	0.028	0.018	0.009
1.00	0.495	0.420	0.350	0.277	0.217	0.158	0.112	0.070	0.045	0.027	0.013
3.16	0.533	0.466	0.400	0.323	0.261	0.203	0.156	0.107	0.076	0.050	0.032
10.0	0.585	0.524	0.462	0.390	0.323	0.265	0.212	0.156	0.118	0.089	0.068
31.6	0.653	0.592	0.533	0.468	0.400	0.334	0.278	0.213	0.175	0.143	0.122
100	0.747	0.681	0.620	0.552	0.480	0.413	0.347	0.280	0.230	0.210	0.183
316	0.860	0.782	0.718	0.644	0.571	0.496	0.429	0.362	0.320	0.287	0.257^a
1000	1.000	0.902	0.830	0.758^a	0.680^a	0.600^a	0.533^a	0.465^a	0.425^a	0.390^a	0.358^a

	α_{H_2S}										
α_{CO_2}	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000
p_{H_2S}											
0.100	0.201	0.156	0.115	0.075	0.043	0.022	...	...	...	...	...
0.316	0.360	0.257	0.186	0.123	0.069	0.029	...	...	...	...	...
1.00	0.530	0.370	0.266	0.182	0.100	0.048	0.019	0.004	...	...	...
3.16	0.700	0.488	0.352	0.246	0.142	0.075	0.039	0.010	...	...	...
10.0	0.832	0.609	0.453	0.315	0.203	0.123	0.073	0.032	0.016	...	...
31.6	0.905	0.703	0.558	0.400	0.283	0.196	0.132	0.080	0.049	0.023	0.009
100	0.984	0.789	0.660	0.518	0.409	0.309	0.243	0.184	0.137	0.082	0.052
300	1.300	0.944	0.793	0.685	0.590	0.487	0.407	0.340	0.274	0.203^a	0.154^a
500	...	1.030	0.920	0.792^a	0.705^a	0.610^a	0.523^a	0.435^a	0.356^a	0.287^a	0.230^a

[a] Extrapolated values.

Table IV. Smoothed Data for Solubility of Mixtures of Acid Gases in 5.0N Monoethanolamine Solution at 100°C

α, mole ratio in liquid, acid gas/MEA; p, partial pressure of acid gas, psia

	α_{CO_2}									
α_{H_2S}	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900
p_{CO_2}										
0.0100	0.067	...	...	...	...	...	...	...	...	...
0.0316	0.100	0.060	0.019	...	...	...	...	...	...	...
0.100	0.143	0.102	0.052	0.026	...	...	...	...	...	...
0.316	0.200	0.153	0.104	0.068	0.040	0.013	...	...	...	...
1.00	0.270	0.219	0.167	0.127	0.093	0.062	...	...	...	...
3.16	0.333	0.285	0.230	0.188	0.150	0.113	0.083	0.059	0.034	0.011
10.0	0.401	0.346	0.293	0.251	0.208	0.166	0.129	0.096	0.065	0.034
31.6	0.473	0.411	0.360	0.313	0.268	0.221	0.676	0.136	0.100	0.063
100	0.552	0.488	0.432	0.380	0.329	0.277	0.229	0.182	0.140	0.098
316	0.642	0.571	0.509	0.450	0.391	0.336	0.289^a	0.232^a	0.186^a	0.138^a
1000	0.752	0.668	0.596	0.528	0.461	0.402	0.350^a	0.294^a	0.243^a	0.191^a

	α_{H_2S}							
α_{CO_2}	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700
p_{H_2S}								
0.100	0.040^a	0.025^a	...	...	...	...	...	...
0.316	0.075^a	0.051^a	0.032^a	0.016^a	...	...	...	...
1.00	0.135	0.094	0.068	0.040	...	...	...	...
3.16	0.233	0.167	0.122	0.082	0.050	0.022	...	...
10.0	0.383	0.270	0.200	0.143	0.095	0.054	0.029	0.006
31.6	0.603	0.414	0.306	0.232	0.166	0.110	0.067	0.032
100	0.790	0.613	0.460	0.352	0.264	0.187	0.127	0.077
300	1.030	0.773	0.640	0.510	0.395	0.288	0.203	0.139
600	...	0.897	0.730	0.632	0.505	0.377^a	0.273^a	0.193^a

[a] Extrapolated values.

Results and Discussion

The equilibrium solubility of mixtures of H_2S and CO_2 in 5.0*N* MEA solution was measured at 40° and 100°C. Partial pressures of CO_2 ranged from 0.1 to 810 psia, and H_2S partial pressures were between 0.1 and 510 psia. Tables I and II (deposited with the ACS Microfilm Depository Service) show the experimental data for 40° and 100°C, respectively. It is not possible to represent the liquid- and gas-phase compositions for both CO_2 and H_2S on a single plot. Thus, the raw data were smoothed by preparing separate plots of the log of the partial pressure vs. the mole ratio of the acid gas to amine in the liquid, α, for both CO_2 and H_2S at a given temperature. Lines of constant α for the second acid gas component were drawn on these plots by eye so that the figures were mutually consistent.

The final plots for 40°C are given as Figures 1 and 2. Figure 1 shows the effect of CO_2 on the partial pressure of H_2S, and Figure 2 the effect of H_2S on the partial pressure of CO_2. Smoothed values for acid gas solubilities are presented in Tables III and IV. The data presented in Tables III and IV are estimated to be accurate to about 0.02 or 4%, whichever is larger, in liquid concentration at a given partial pressure of acid gas. No comparisons with data from literature are possible for this solution.

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Received for review May 17, 1974. Accepted November 4, 1974. Work supported by the Canadian Natural Gas Processing Association and the National Research Council of Canada.

Supplementary Material Available. Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JCED-75-161.

Liquid-Liquid Phase Equilibria for Ternary Systems Hexamethyldisiloxane-Acetic Acid (Propionic Acid)-Water

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Liquid-liquid phase equilibria in the ternary systems hexamethyldisiloxane–acetic acid (propionic acid)–water were studied. Tie lines of two-phase conjugate layers were determined by use of a cross-section method. Partition coefficients were calculated for acetic acid and propionic acid between the aqueous and hexamethyldisiloxane phase. Their mean values were 2.21 and 0.913, respectively, at 20° ± 1°C.

Phase equilibria in multicomponent systems have been extensively studied (*3*). However, those comprising hexamethyldisiloxane as one of the components have been given little attention. To our knowledge, there is only one report in the literature confined to the study of equilibrium for a system comprising hexamethyldisiloxane (*5*). In this work the solubility of hexamethyldisiloxane in acidic media has been studied. The compound is fairly resistant to hydrolysis and possesses properties which may be utilized in extraction and chromatography (*2, 4, 5, 7*).

Materials

The materials were of reagent grade, redistilled before being used to ensure uniform properties. A fraction of hexamethyldisiloxane (HMDS) boiling at 99.5–100.5°C was collected ($d^{20}{}_4$ 0.7636, $n^{20}{}_D$ 1.3774). The bp of acetic acid was 118.5–119°C ($d^{20}{}_4$ 1.0497, $n^{20}{}_D$ 1.3714), and that of the propionic acid was 141–142°C ($d^{20}{}_4$ 0.9941, $n^{20}{}_D$ 1.3863).

Procedure

Liquid-liquid phase equilibria were investigated by use of the method of isothermic titration developed by Bancroft (*1*). For the system comprising acetic acid, 11 binary solutions of HMDS and the acid, of various concentrations, were prepared, and for that comprising propionic acid, 17 binary solutions. The solutions were then titrated with water by use of a microburet until a slight turbidity appeared. During the titration, samples were shaken and thermostated to within 20° ± 1°C. Three titrations were accomplished for each sample, and mean results were taken.

Analysis of Phase Composition

To determine tie lines of conjugate layers, ternary two-phase systems were analyzed by the so-called cross-section method reported by Nikurashina et al. (*6*). It consists in plotting the refractive index of a mixture against concentration of one of the components at a constant ratio of the remaining two components. As known, secants A, B, and C (Figure 1 and 2), developed from a point of a triangle representing acid concentration in a mixture, are loci of points characterized by a constant ratio of concentrations of the remaining two components.

If for each secant a series of mixtures is prepared which occur in a two-phase region and differ in the acid content, and the refractive indices of one of the equilibrium phases are measured, one obtains a relationship between the refractive index and acid concentration for a given phase (Figure 3). Since the composition of equilib-

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