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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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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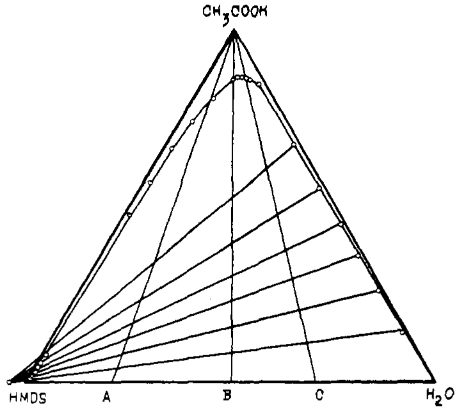

Figure 1. Solubility curve for system hexamethyldisiloxane-acetic acid-water

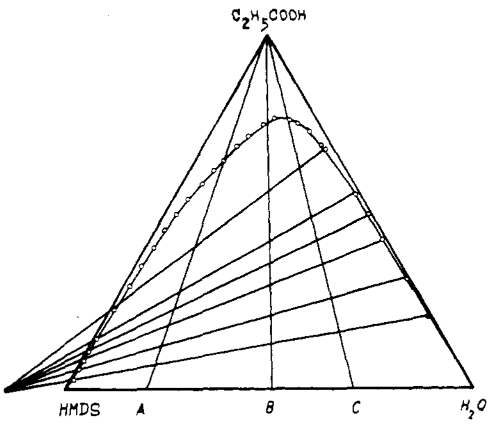

Figure 2. Solubility curve for system hexamethyldisiloxane-propionic acid-water

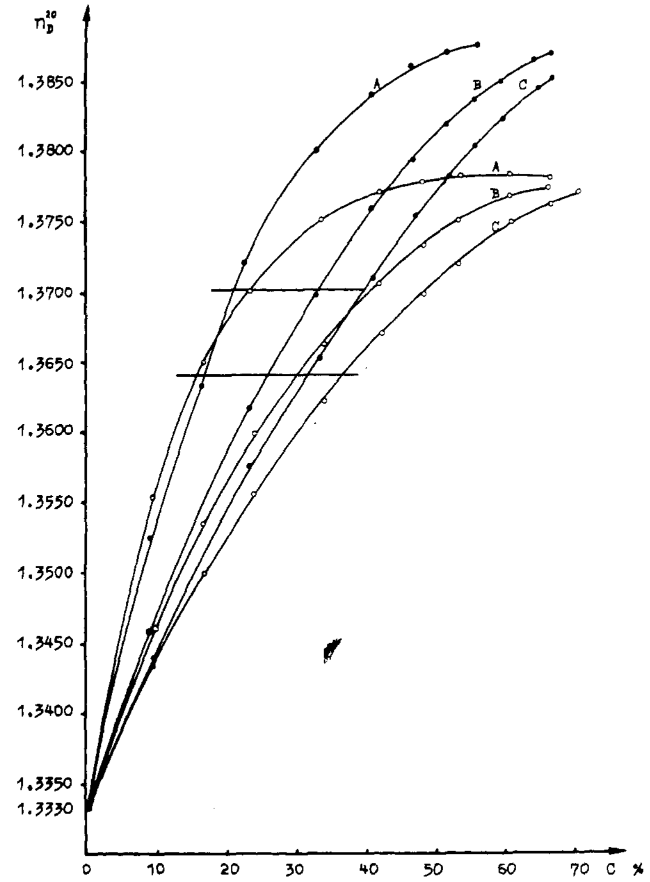

Figure 3. Plots of n^{20}_D vs. concentration of acetic acid (O) and propionic acid (●). Curves A, B, and C correspond to secants in a triangular diagram for which HMDS:H_2O ratios are 80:20, 50:50, and 30:70, respectively

rium phases lying on one tie line is constant, their refractive index values must also be constant. Hence, arbitrary values of the refractive index (e.g., 1.3640 and 1.3700 as shown in Figure 3) may be chosen in a plot of $n_D = f(c_{acid})$ which indicates on the curves the corresponding points determining the acid content in the phases considered. The points lie on three secants (A, B, and C), but they belong to the same tie lines. To plot six tie lines in Figure 1, the following six values of the refractive index were taken from Figure 3: 1.3445, 1.3525, 1.3605, 1.3640, 1.3700, and 1.3755. Concentrations of acetic acid taken from Figure 3 were then plotted in Figure 1 to give tie lines for individual refractive index values. The smallest value corresponds to the first tie line situated at the base of the triangle. A similar procedure was used for plotting tie lines shown in Figure 2.

Composition of the conjugate layers is read from intersections of the tie lines with a binodal curve illustrating the equilibrium between a one- and a two-phase system.

Results

In Figure 3 relationships are presented between refractive index and concentrations of the acids in the lower (aqueous) phase in the two ternary systems studied.

Binodal curves composed of points representing the composition of ternary mixtures at the moment of the onset of turbidity are shown in Figures 1 and 2, and the relevant data are given in Table I. In the figures, tie lines are shown as well. In both systems, limiting concentrations of the binary solutions were observed in which water had been dissolved. At concentrations of acetic acid lower than 40% (v/v), the turbidity appeared after addition of one drop of water. A similar phenomenon was observed in the second system with propionic acid concentrations lower than 25% (v/v). On the other hand, HMDS was completely immiscible with water.

Table I. Solubility Data of Ternary Systems at 20°C (Composition in Wt %)

No.	HMDS	CH_3-COOH	H_2O	HMDS	CH_3CH_2-COOH	H_2O
1	1.27	85.37	13.36	2.22	69.26	28.52
2	2.63	86.63	10.74	3.62	73.80	22.58
3	3.31	86.61	10.07	5.08	76.11	18.86
4	4.06	87.51	8.42	6.58	77.06	16.36
5	5.52	87.33	7.14	10.48	77.34	12.17
6	6.69	86.51	6.50	14.41	75.03	10.57
7	14.70	80.87	4.43	18.60	72.64	8.77
8	23.19	74.38	2.43	22.91	69.60	7.50
9	32.04	66.07	1.89	27.29	65.98	6.74
10	41.65	57.26	1.09	32.02	62.54	5.45
11	51.82	47.50	0.68	36.90	58.71	4.40
12				42.01	54.69	3.30
13				47.25	50.33	2.36
14				52.50	45.56	1.95
15				58.10	40.73	1.17
16				63.65	35.52	0.83
17				69.23	30.05	0.73

Conclusions

The shape of binodal curves (Figures 1 and 2) resembles that of an asymmetric parabola. The asymmetry is likely to be due to differences in solubility of the acids in water and in HMDS.

The two-phase systems (lower area of the triangular diagram) separated into two layers. The upper one contained mostly HMDS, a small amount of the acid, and a very small amount of water, whereas the lower one comprised water as the main component, followed by the acid and a very small amount of HMDS.

In this work, the suitability of the cross-section method (Figure 3) has been demonstrated for determining tie lines of conjugated systems. The lines intersect at one point lying on the extension of one side of a triangle representing the composition of immiscible components.

Results of analyses of the conjugated layers allowed us to determine partition coefficients of the acids between the aqueous and HMDS phases. Their mean values were 2.21 and 0.913 for the acetic and propionic acid, respectively, at 20° ± 1°C.

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pH Dependence on Composition of Aqueous Solution Saturated with Sodium Phosphate, Sodium Chloride, and Sodium 5′-Inosinate

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The composition data of the aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate were obtained between pH 2 and 11 at 10° and 30°C, respectively. Those in the absence of sodium chloride were also obtained. The salting-out effect of sodium phosphate on sodium chloride or on sodium 5′-inosinate is clearly demonstrated. Sodium chloride also showed a salting-out effect on disodium 5′-inosinate.

For the industrial production of disodium 5′-inosinate (disodium inosine-5′-monophosphate, 5′-IMP·Na_2), an excellent flavor enhancer, phosphorylation of inosine with an excess of phosphoryl chloride is eminently useful (*6*, *7*). In this reaction, however, a by-product of phosphoric acid and hydrochloric acid is inevitable as shown in the following equation:

$$\text{Inosine} + n\cdot POCl_3 + [2 + 3(n-1)]\cdot H_2O \rightarrow 5'\text{-IMP}\cdot H_2 + (n-1)\cdot H_3PO_4 + 3n\cdot HCl$$

where $n > 1$. After neutralization with sodium hydroxide to various pH values, crystallization of sodium 5′-inosinate can be performed in the presence of sodium phosphate and sodium chloride.

This paper describes the pH dependence on the composition of the aqueous solution saturated with sodium phosphate, sodium chloride, and sodium 5′-inosinate at 10° and 30°C, respectively. No data have been previously reported involving these systems.

Experimental

Disodium 5′-inosinate octahydrate (5′-IMP·Na_2·$8H_2O$) was obtained through recrystallization of commercial "IN" (Ajinomoto Co., Inc.) in water. The melting point was 118–120°C (rapid heating in a capillary, uncorrected). The water content by Karl Fischer method (3), 26.5%: Calcd for $8H_2O$, 26.9%. The molar extinction coefficient at 250 nm in 0.1*N* HCl, 11,500.

Monosodium 5′-inosinate tetrahydrate (5′-IMP·NaH·$4H_2O$) was prepared according to Suzuki et al. (*5*). The melting point was 108–111°C (rapid heating in a capillary, uncorrected). The water content by Karl Fischer method (*3*), 16.3%: Calcd for $4H_2O$, 16.3%. The molar extinction coefficient at 250 nm in 0.1*N* HCl, 11,500. Other materials were obtained commercially (GR reagent grade). 5′-Inosinic acid was determined by measurement of the ultraviolet absorbance at 250 nm in 0.1*N* HCl, using the tentative molar extinction coefficient of 11,500. Phosphoric acid was determined by a phosphovanadomolybdate method (*2*). Sodium chloride was determined by the Volhard method (*1*).

Samples were allowed to reach equilibrium in a constant-temperature bath maintained at ±0.5°C. The pH of the solutions was measured by a Toa Dempa pH meter Model HM-5A. The electrode was standardized with two buffer solutions. In the acidic pH measurement a phosphate buffer solution (pH 6.86) and a phthalate buffer solution (pH 4.01) were adopted, whereas in the alkaline pH measurement a phosphate buffer solution (pH 6.86) and a borate buffer solution (pH 9.18) were used.

Several kinds of the materials were added to water to make a slurry in a tightly capped glass bottle. The cap was also made of glass. Dissolution and equilibration were achieved by tumbling the bottles for at least 16 hr at 10° or 30°C. No indications of bacterial growth were found at 30°C/16 hr, probably because the concentration of the solution was too high. After equilibration the pH of the solution was measured, and the liquid phase was separated from the solid phase by filtration. Each portion of the filtrates and the wet residues was sampled, diluted, and analyzed, respectively.

The method of slurry making was as follows: In a region below pH 4.0, an excess amount of 5′-IMP·NaH·