Liquid-Vapor Equilibria of Binary Systems of Hexamethyldisiloxane with Some Carboxylic Acids

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Phase equilibria were studied in the systems hexamethyldisiloxane (HMDS)–acetic acid, HMDS–propionic acid, and HMDS–butyric acid under isobaric and isothermal conditions. In the first-named system an azeotrope was observed at 0.485 mole fraction acetic acid, boiling at 95.8°C at 764 mm Hg. The maximum vapor pressure of the azeotrope was equal to 38 mm Hg at 20°C. The two remaining systems were zeotropic mixtures.

Studies concerning phase equilibria are indispensable for the development of some technological processes. Liquid-vapor equilibrium relationships are especially important properties of liquid mixtures, and isobaric data in particular are required for practical use, such as in the design and operation of distillation equipment.

To our knowledge, reports concerning phase equilibria of systems comprising hexamethyldisiloxane (HMDS) are rather scarce. In 1966 a paper appeared on vapor-liquid equilibrium for the HMDS–*n*-propyl alcohol system (*3*), and in 1973 a thesis of Guzman (*2*) was confined to vapor-liquid equilibrium relationships in nonideal binary systems HMDS–toluene, HMDS–ethyl alcohol, and ethyl alcohol–toluene.

In this work, binary systems have been studied comprising HMDS and a lower fatty acid. The components form homogeneous mixtures.

Materials

Both HMDS and the acids used were pure commercial products, additionally purified by fractional distillation. Their physical constants are given in Table I.

Procedure

For each of the systems studied, nine solutions were prepared with HMDS/acid mole ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 8:2, and 9:1 which covered the whole concentration range. The components were mixed together by means of a buret with an accuracy of ±0.01 cm^3. The relationship between boiling point and composition was determined with the Swietoslawski ebulliometer (*5*). Total vapor pressure was measured by a static method with an apparatus reported by Szarawara and Buczek (*6*) and shown in Figure 1. The apparatus consists of a 300-cm^3 round-bottomed vacuum flask 1, of another flask 2 of the same capacity, and of three manometers 3, 4, and 5. The equipment also involves a vacuum pump and a thermostat in which flask 1 and manometer 4 are immersed.

Before beginning the measurement, air was removed from the apparatus, the temperature of the thermostat was brought to a required level, and a sample was placed in flask 2. Then the sample was transferred to flask 1. Vapor pressure of the substance caused a change in mercury levels in manometer 4. The levels were then equaled by admission of air through a stopcock. This affected readings of manometer 3. A difference in readings in manometer 3 before and after the measurement gave vapor pressure of the sample:

$$\Delta h = h_2 - h_1$$
$$p = b - \Delta h$$

where h_2 is the height of mercury in the right arm of manometer 3, h_1 is the height of mercury in the left arm of the manometer, p is equilibrium pressure, and b is atmospheric pressure read out in manometer 3 before the measurement.

Although the readings are taken directly, results show systematic errors which can readily be eliminated by carrying out measurements with a standard liquid.

The composition of the liquid and the condensate was determined refractometrically, based on previously constructed calibration graphs. Isothermal measurements were run at 20° ± 0.1°C, and the vapor pressure was measured with an accuracy of 0.5 mm Hg. In isobaric experiments (under atmospheric pressures indicated in the captions of Figures 2–4) the temperature was measured with an accuracy of ±0.2°C with a mercury thermometer. Density was estimated pycnometrically with a 10-cm^3 pycnometer calibrated with water. The pycnometer was thermostated at 20° ± 0.1°C. Results are shown in Figures 2–4. Total vapor pressures under isothermal conditions are shown in Figures 5–7. In these figures are also plotted deviations from the additivity rule of refractive indices and densities ($\Delta n^{20}{}_D$ and $\Delta d^{20}{}_4$, respectively) which are indicative of intermolecular interactions between the components.

Numerical data on liquid-vapor equilibria in binary systems under isobaric conditions are presented in Table II. Total vapor pressures, densities, and refractive indices of the systems studied are shown in Table III.

Discussion of Results and Conclusions

The results of both isothermal and isobaric measurements show the occurrence of a positive deviation from Raoult's law for all of the systems studied. Accordingly, the interaction be-

Table I. Physical Properties of Materials

	Boiling point, °C		Density at 20°C, g/cm³		Refractive index	
Material	Exptl	Lit	Exptl	Lit	Exptl	Lit
HMDS	101–102	99–101 (*7*)	0.7619	0.7619 (*4*)	1.3777	1.3772 (*7*)
Acetic acid	118–119	117.897 (*1*)	1.0498	1.0492 (*8*)	1.3715	1.3716 (*8*)
Propionic acid	141–142	139.402 (*1*) 141.22–141.35 (*8*)	0.9942	0.9934 (*8*)	1.3862	1.3865 (*8*)
Butyric acid	163–164	163.279 (*1*)	0.9587	0.9580 (*8*)	1.3980	1.39796 (*8*)

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tween the molecules of the acids and HMDS is weaker than that between the molecules of each of the components. This finding is consistent with the tendency of carboxylic acids to associate in nonpolar liquids.

In the system HMDS–acetic acid, a minimum boiling point (95.8°C) is observed at 764 mm Hg and corresponds to a positive azeotrope containing 0.485 mole fraction acetic acid. Under isothermal conditions a maximum of vapor pressure occurs and is equal to 38 mm Hg.

The systems HMDS–propionic acid and HMDS–butyric acid do not form azeotropes under isothermal and isobaric conditions. They may be ranged among positive zeotropes.

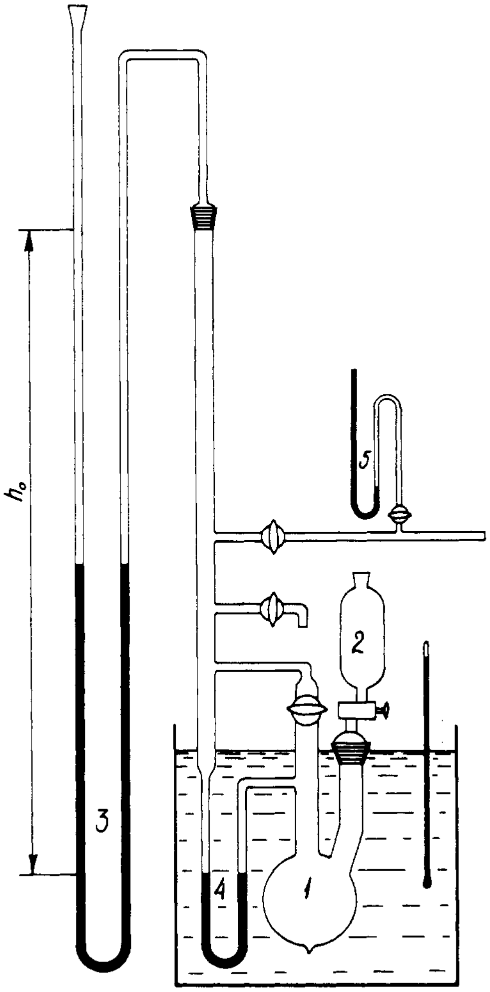

Figure 1. Apparatus used for measurement of total vapor pressure (*6*)

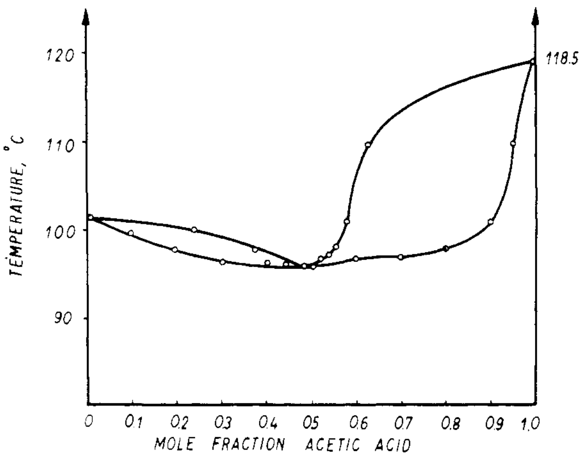

Figure 2. Boiling point vs. composition for system HMDS–acetic acid at 764 mm Hg

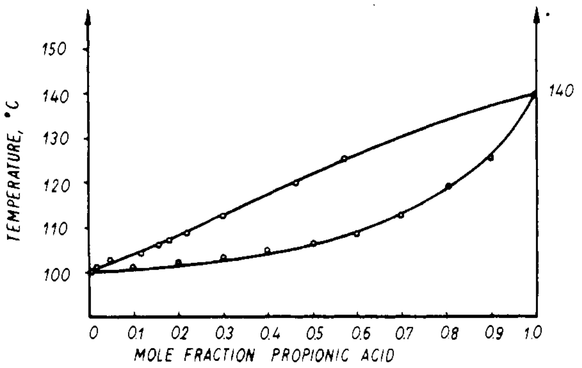

Figure 3. Boiling point vs. composition for system HMDS–propionic acid at 742 mm Hg

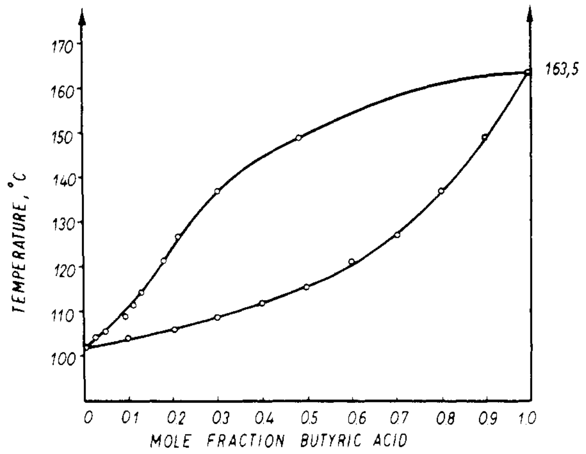

Figure 4. Boiling point vs. composition in system HMDS–butyric acid at 766 mm Hg

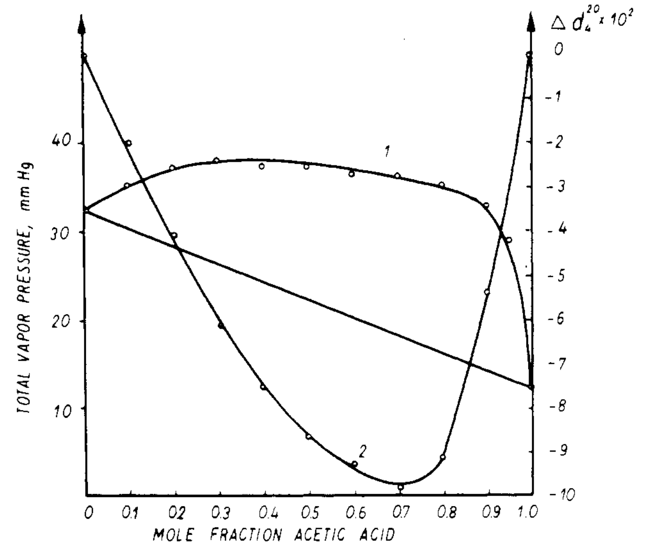

Figure 5. Total vapor pressure (curve 1) and differences between observed and calculated values of densities ($\Delta d^{20}{}_4$, curve 2) for system HMDS–acetic acid

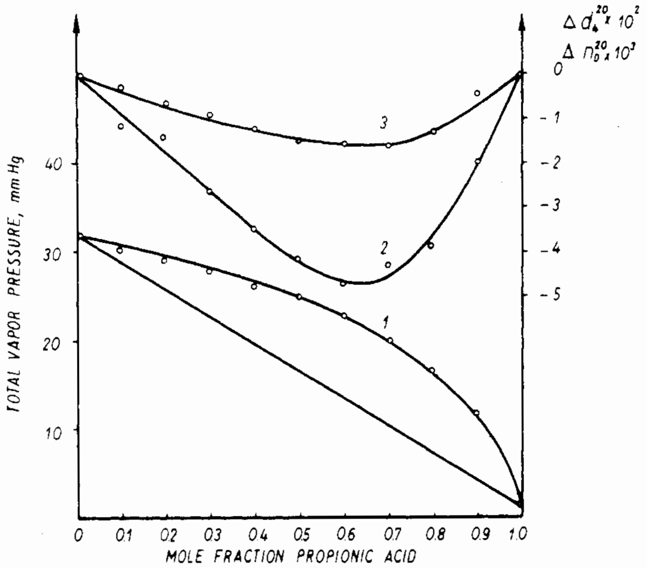

Figure 6. Total vapor pressure (curve 1) and differences between observed and calculated values of densities (Δd^{20}_4, curve 2) and refractive indices (Δn^{20}_D, curve 3) for system HMDS–propionic acid

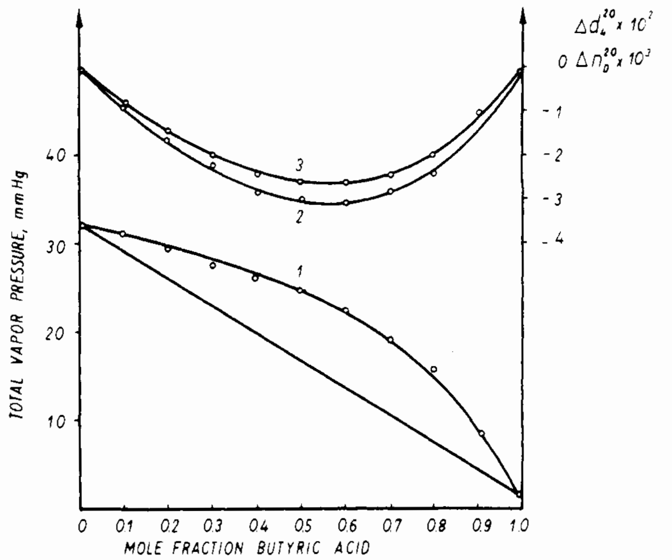

Figure 7. Total vapor pressure (curve 1) and differences between observed and calculated values of densities (Δd^{20}_4, curve 2) and refractive indices (Δn^{20}_D, curve 3) for system HMDS–butyric acid

Table II. Liquid-Vapor Equilibrium Data for Binary Systems Under Isobaric Conditions

	HMDS–acetic acid			HMDS–propionic acid			HMDS–butyric acid		
No.	x^a	y^b	t, °C	x	y	t, °C	x	y	t, °C
1	0.9	0.76	99.5	0.9	0.98	102.6	0.9	0.97	104.0
2	0.8	0.615	97.7	0.8	0.95	103.1	0.8	0.95	105.1
3	0.7	0.6	96.4	0.7	0.88	105.0	0.7	0.9	108.3
4	0.6	0.557	96.0	0.6	0.84	106.7	0.6	0.89	111.1
5	0.5	0.515	95.8	0.5	0.82	107.2	0.5	0.875	114.1
6	0.4	0.475	96.7	0.4	0.78	109.5	0.4	0.82	120.7
7	0.3	0.46	96.9	0.3	0.70	113.3	0.3	0.79	126.6
8	0.2	0.445	97.7	0.2	0.54	120.5	0.2	0.70	136.0
9	0.1	0.415	100.8	0.1	0.43	126.4	0.1	0.515	148.2
10	0.05	0.375	109.7	0.0	0.0	140.0	0.0	0.0	163.5
11	0.0	0.0	118.5						

[a] Mole fraction HMDS in the liquid phase. [b] Mole fraction HMDS in the vapor phase.

Table III. Refractive Indices, $n^{20}D$, Densities, d^{20}_4, and Total Vapor Pressures (p in mm Hg) for Binary Systems

		HMDS–acetic acid			HMDS–propionic acid			HMDS–butyric acid		
No.	x^a	$n^{20}D$	d^{20}_4	p^{20}	$n^{20}D$	d^{20}_4	p^{20}	$n^{20}D$	d^{20}_4	p^{20}
1	0.9	1.3770	0.7700	35.4	1.3783	0.7839	30.5	1.3788	0.7703	30.0
2	0.8	1.3764	0.7778	37.0	1.3787	0.7939	29.0	1.3802	0.7899	29.0
3	0.7	1.3757	0.7866	38.1	1.3793	0.8059	28.2	1.3818	0.8016	27.3
4	0.6	1.3751	0.8018	37.2	1.3798	0.8192	25.8	1.3833	0.8107	26.0
5	0.5	1.3744	0.8180	37.0	1.3805	0.8358	25.0	1.3852	0.8294	25.0
6	0.4	1.3737	0.8416	36.0	1.3812	0.8537	23.5	1.3872	0.8489	21.8
7	0.3	1.3730	0.8645	36.0	1.3820	0.8892	20.0	1.3894	0.8724	19.1
8	0.2	1.3724	0.9010	35.2	1.3832	0.9091	17.0	1.3919	0.8912	16.2
9	0.1	1.3721	0.9667	33.5	1.3849	0.9480	12.0	1.3949	0.9327	8.0
10	0.05	1.3720	0.9950	29.0	...	...	...	...	...	...
11	0.0	1.3715	1.0498	12.0	1.3864	0.9942	1.0	1.3979	0.9587	0.8

[a] Mole fraction HMDS in binary solutions.

Moreover, the systems studied show negative deviations of refractive indices and densities from the additivity rule. The largest deviation is observed in the system HMDS–acetic acid, where a minimum of $\Delta d^{20}{}_4$ amounts to 10.27% and occurs at the mole fraction acetic acid of 0.7. However, the deviations of refractive indices are generally small. Only for the mole fraction 0.7 of acetic acid, the deviation exceeds the experimental error and reaches 0.026%.

The largest differences in the composition of the liquid and the vapor phases are observed in the system HMDS–butyric acid. The components of the system may thus be most readily separated by fractional distillation.

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Received for review November 19, 1974. Accepted April 18, 1975.

Drag Reduction Characteristics of Poly(acrylamides) in Aqueous Magnesium Sulfate and Acetone Solutions

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The drag reduction efficiency of four commercial poly(acrylamide) samples was determined in water and aqueous solutions of acetone and magnesium sulfate. Intrinsic viscosity measurements were made in the magnesium sulfate solutions over the shear rate range of 15–100 sec^{-1}. In general, increasing concentrations of salt or acetone produced progressive decreases in the drag reducing efficiencies of these polymers. In contrast to the data previously obtained with the poly(ethylene oxide) polymers in salt solutions, no simple relation between the drag reduction efficiency and intrinsic viscosity could be established as the salt concentration was varied. The data do show, however, that the drag reduction efficiency of poly(acrylamide) is much less affected by increases in salt concentration than is the efficiency of poly(ethylene oxide).

The drag reduction characteristics of an important nonionic polymer, poly(ethylene oxide) (PEO) in solutions of varying salt content have been successfully correlated with the intrinsic viscosity of the polymer in those solutions (*9*). It was suggested that those solvent properties which bring about decided conformational changes in these polymer molecules also affect, in an apparently analogous fashion, the turbulent friction reducing efficiencies of these same molecules. However, these conclusions were specific to nonionic polymer solutions. Changes in drag reduction and reduced viscosity do not necessarily go hand-in-hand in polyelectrolyte solutions, the effect of pH on the performance of polyacrylic acid being specifically cited as evidence for this conclusion (*5*). Clarke (*2*) has reported the behavior of two commercial samples of poly(acrylamide) (PAM) in water, 0.02 and 1.0*M* sodium chloride. He noted very high intrinsic viscosities in water (shear rate unspecified) for both the slightly hydrolyzed and 33% hydrolyzed PAM samples. He further stated that the ionic nature of the polymer did not directly affect its drag reducing properties and could be explained in terms of the usual drag reduction characterization procedures.

Frommer et al. (*3*), on the other hand, have made drag reduction and reduced viscosity measurements on a hydrolyzed commercial PAM sample in a series of low molarity barium chloride solutions. Their data suggest that a rough parallelism exists between the two sets of data in the low molarity range. However, it may be of further interest to expose PAM samples of varying molecular weight and type to environments which contain high concentrations of ions, particularly those which are divalent, observing any effect on the drag reducing efficiencies of these polymers. It may also be of further value to compare these results with those previously reported for PEO to determine the relative merits of each family in hostile ionic environments.

Experimental

Materials. The following commercial poly(acrylamides) were selected: Separan NP-20 (Dow), Cyanamer P-250 (American Cyanamide), and two samples of Magnifloc 905N (American Cyanamide). According to the manufacturers, Separan NP-20 is mildly nonionic with 3.9% of the monomer units charged; Cyanamer P-250 and Magnifloc 905N are advertised as pH-insensitive with regard to their viscosities and are therefore supposedly nonionic in nature. Freshly distilled water was used exclusively in preparing all solutions. Since irreproducible mixing techniques can cause large variations in solution properties, all solutions were prepared carefully by the following procedures.

The additives in powder form were sprinkled uniformly over a large surface of distilled water to avoid clumping of particles. Solution was allowed to take place through diffusion at 6°C for a period of several days. Occasional gentle stirring with a glass rod ensured adequate dispersion of solute. To obtain the desired concentration of polymer, a stock solution of reagent grade magnesium sulfate was slowly added with gentle stirring to the required amount of polymer solution. Stock solutions of polymer were always stored at 6°C and were discarded after a two-week period. The pH of all solu-

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