sistency as indicated in Figure 6 by the Othmer-Tobias coordinate (*11*).

Acknowledgment

The authors wish to express their sincere thanks to Dr. I. B. Gulati, Director, for the encouragement from time to time.

Glossary

X	liquid-phase composition, weight fraction

Subscripts

1	*n*-heptane
2	solvent
3	benzene
11	composition (weight fraction) of component 1 in phase 1 (*n*-heptane-rich phase)
22	composition (weight fraction) of component 2 in phase 2 (solvent-rich phase)

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Liquid-Vapor Equilibria in Binary Systems of Hexamethyldisiloxane-1-Butanol, -2-Butanol, and -2-Methyl-1-propanol

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Liquid-vapor phase equilibria have been studied under isobaric conditions, and total vapor pressures were measured at 20 °C. In the three binary systems studied, large positive deviations from the ideal behavior have been observed. An azeotrope in the hexamethyldisiloxane (HMDS)-1-butanol system was formed at 0.725 mole fraction HMDS at 765 mmHg. In the hexamethyldisiloxane-2-methyl-1-propanol system the minimum boiling point occurred at 0.615 mole fraction HMDS at 766 mmHg. In the third binary system, an azeotrope contained 0.540 mole fraction HMDS at 754 mmHg.

A variety of physicochemical techniques, including ebulliometry, have been employed for studying intermolecular interactions. As there are only a few reports in the literature (*1-3*) on molecular interaction between hexamethyldisiloxane and alcohols, this work has been confined to the measurements of vapor pressures and boiling points in the systems including hexamethyldisiloxane and isomeric butanols. Results of these measurements can provide a basis for evaluation of the nature of deviation of the systems from ideal state.

Experimental Section

Materials. Prior to measurements all reagents were purified by repeated distillation. Their boiling points (bp), densities (d^{20}_4) and refraction indices (n^{20}_D) were as follows: hexamethyldisiloxane (HMDS) bp 100-100.5 °C, d^{20}_4 0.7636 g cm^{-3}, n^{20}_D 1.3774; 1-butanol bp 118 °C, d^{20}_4 0.8104 g cm^{-3}, n^{20}_D 1.3987; 2-butanol bp 99-100 °C, d^{20}_4 0.8080 g cm^{-3}, n^{20}_D 1.3972; 2-methyl-1-propanol bp 108-109 °C, d^{20}_4 0.8020 g cm^{-3}, n^{20}_D 1.3958.

Procedure. For each of the systems studied, a series of solutions was prepared by covering the whole concentration range of both components.

Table I. Liquid-Vapor Equilibria under Isobaric Conditions, Total Vapor Pressure, *P*, Density d^{20}_4, and Refractive Index n^{20}_D in the Systems Hexamethyldisiloxane-Butyl Alcohols

	HMDS mole fraction				
temp, °C	vapor	liquid	d^{20}_4	n^{20}_D	*P*, mmHg (20 °C)
P = 765 mmHg	Hexamethyldisiloxane-1-Butanol				
98.4	0.840	0.904	0.7661	1.3788	37.0
97.2	0.772	0.795	0.7698	1.3801	37.5
97.0	0.725	0.725	0.7736	1.3817	37.8
97.5	0.719	0.610	0.7786	1.3836	35.5
98.1	0.690	0.500	0.7826	1.3856	35.0
99.3	0.675	0.404	0.7856	1.3878	34.0
100.6	0.648	0.299	0.7916	1.3904	30.5
103.9	0.622	0.200	0.7976	1.3932	26.0
109.2	0.530	0.102	0.8024	1.3962	21.4
118.0		0.000	0.8104	1.3992	6.0
P = 766 mmHg	Hexamethyldisiloxane-2-Methyl-1-propanol				
97.9	0.815	0.902	0.7677	1.3784	35.0
96.6	0.743	0.800	0.7724	1.3791	35.2
95.0	0.645	0.692	0.7756	1.3804	35.4
94.6	0.615	0.615	0.7789	1.3819	35.5
95.1	0.580	0.507	0.7832	1.3837	35.0
95.3	0.535	0.493	0.7880	1.3852	32.5
96.5	0.480	0.300	0.7919	1.3874	30.0
99.0	0.400	0.205	0.7956	1.3899	27.4
102.6	0.310	0.100	0.7987	1.3928	22.1
108.0		0.000	0.8020	1.3958	8.0
P = 754 mmHg	Hexamethyldisiloxane-2-Butanol				
97.0	0.730	0.895	0.7664	1.3782	36.8
93.2	0.645	0.792	0.7712	1.3792	36.9
91.9	0.590	0.700	0.7715	1.3804	37.0
91.4	0.560	0.604	0.7775	1.3818	37.3
91.2	0.540	0.540	0.7777	1.3827	37.5
91.3	0.520	0.503	0.7784	1.3832	35.5
91.7	0.500	0.409	0.7833	1.3853	35.0
92.3	0.472	0.297	0.7878	1.3877	32.5
93.7	0.404	0.201	0.7933	1.3902	30.5
96.3	0.325	0.105	0.8010	1.3946	25.0
100.0		0.000	0.8080	1.3972	12.0

Total vapor pressure of the systems was measured in a device reported by Szarawara (*4*, *5*). Before each measure-

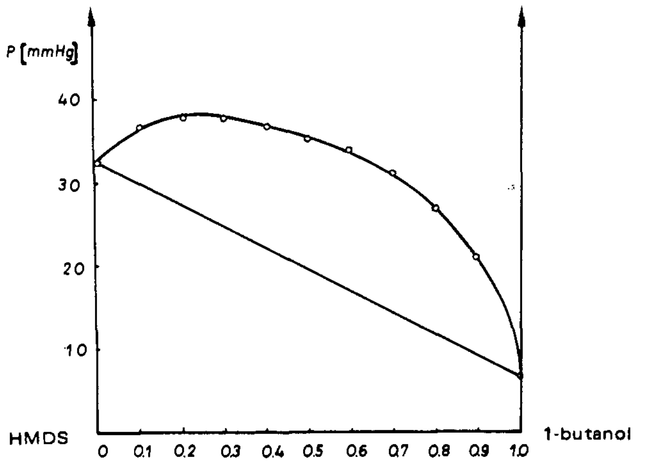

Figure 1. Total vapor pressure for the system hexamethyldisiloxane-1-butanol at 20 °C.

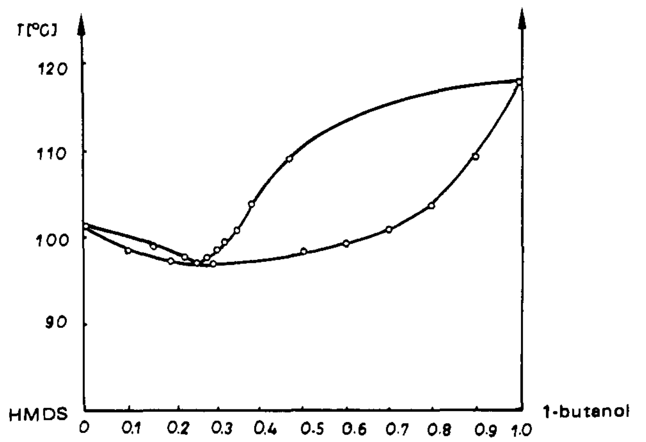

Figure 2. Boiling point vs. composition for the system hexamethyldisiloxane-1-butanol at 765 mmHg.

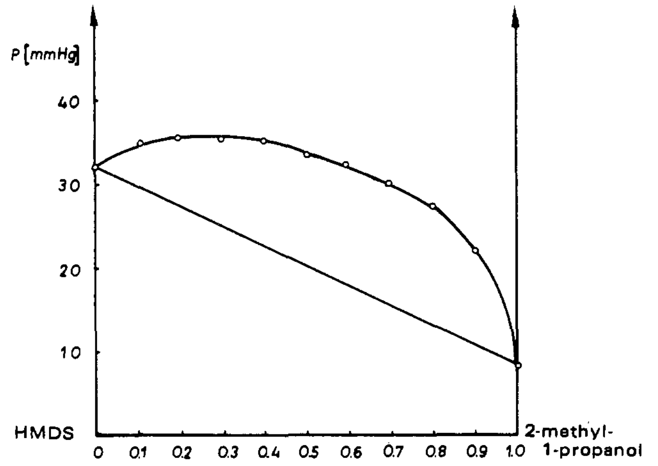

Figure 3. Total vapor pressure for the system hexamethyldisiloxane-2-methyl-1-propanol at 20 °C.

ment the device was checked by using benzene-toluene mixtures.

The measurements were run with a thermostat set at 20 ± 0.05 °C.

Liquid-vapor equilibria under isobaric conditions were measured in a modified Swietoslawski ebulliometer (*6-8*). The compositions of equilibrium liquids and condensed vapor phases were determined refractometrically on the basis of experimental graphs of n^{20}_D vs. composition.

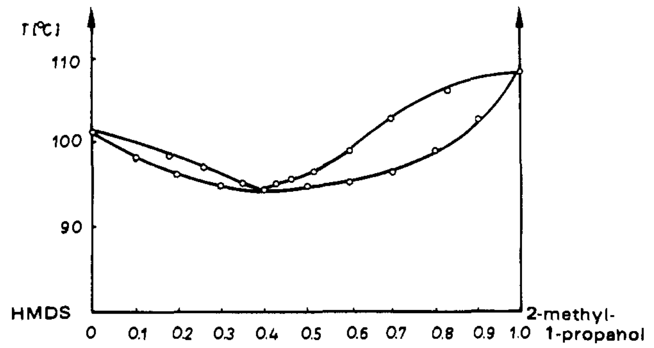

Figure 4. Boiling point vs. composition for the system hexamethyldisiloxane-2-methyl-1-propanol at 766 mmHg.

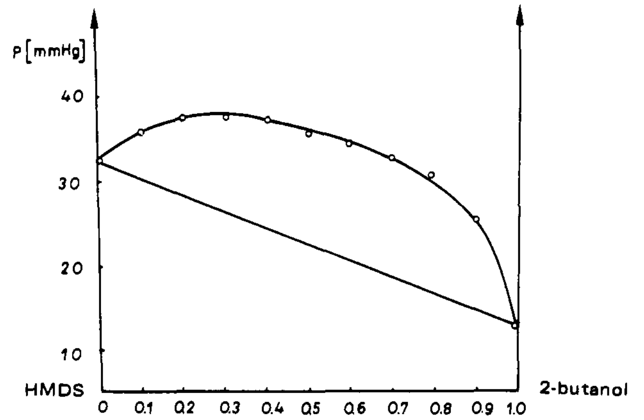

Figure 5. Total vapor pressure for the system hexamethyldisiloxane-2-butanol at 20 °C.

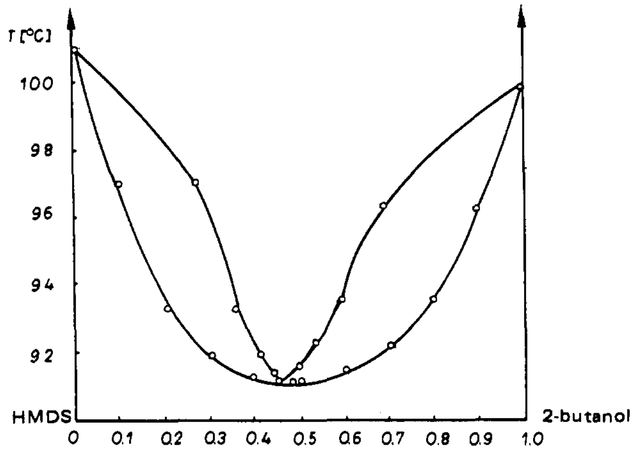

Figure 6. Boiling point vs. composition for the system hexamethyldisiloxane-2-butanol at 754 mmHg.

Results and Conclusions

The results of determination of phase equilibria under isothermal and isobaric conditions in the hexamethyldisiloxane-1-butanol, hexamethyldisiloxane-2-methyl-1-propanol, and hexamethyldisiloxane-2-butanol systems are shown in Table I and in Figures 1-6.

The results of the study of liquid-vapor equilibria reveal large positive deviations from ideal behavior. In all of the systems studied azeotropic mixtures were found. Minimum boiling points under isobaric conditions in Figures 2, 4, and 6 correspond to maximum vapor pressures in the isotherms shown in Figures 1, 3, and 5.

The composition of positive azeotropes under atmospheric pressure has been listed in Table I. The location of the azeotropic mixtures over the HMDS concentration range 0.540-0.725

mole fraction is favorable for observation of variations in volatility of the components after transgression of the azeotropic point. Hexamethyldisiloxane is characterized by a remarkable vapor pressure (32 mmHg at 20 °C) as compared with those of the alcohols studied which have boiling points close to that of hexamethyldisiloxane.

The boiling point of HMDS is only 7 °C lower than that of 2-methyl-1-propanol, whereas the vapor pressure of HMDS at 20 °C is fourfold higher than that of the alcohol. The difference in volatility is still higher with 2-butanol. In this pair of components a slightly lower boiling point of the alcohol is accompanied by its lower vapor pressure at 20 °C. This is indicative of the phenomenon of association of the molecules of alcohol.

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Volumetric Properties of Molten Hydrated Salts. 4. Calcium and Cadmium Nitrate Tetrahydrate with Silver Nitrate

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Densities of molten calcium and cadmium nitrate tetrahydrates with silver nitrate were measured at temperatures ranging between 293.2 and 363.2 K. Densities of mixtures varied linearly with temperature and could be fitted into the equation $\rho = A - B(T - 300)$, coefficients A and B being the characteristic of composition. The systems obeyed the principle of additivity of volumes.

Introduction

The low-temperature molten hydrated salt systems have been studied by several investigators (*1*–*12*, *14*–*21*). Apart from the theoretical interest, these systems are of potential use as a medium for thermal and electrochemical energy storage systems, fuel cells, and low-temperature protonic semiconductors. In continuation of our studies of mass and transport behavior in these systems (*3*, *18*–20), the results of density measurement in molten mixtures of (Ca, Cd)$(NO_3)_2 \cdot 4H_2O$ + $AgNO_3$ are presented in this paper.

Experimental Section

Calcium amd cadmium nitrate tetrahydrates were AnalaR (BDH) grade. The water content of the hydrated salts was determined by volumetric titration using EDTA and found to be within ±0.01 (moles per mole of cation) of their stoichiometric value. Silver nitrate, AnalaR (BDH), was vacuum desiccated in a black painted desiccator to constant mass before use.

A manometeric densitometer (*18*) was used to measure the volume of a known mass of melt with a precision of ±0.001 cm^3. Details of the experimental technique, calibration and precision of data, etc. have been described earlier (*18*). Temperature of the thermostat was maintained constant and known with a precision of ±0.05 K.

Results and Discussion

The densities of molten $Ca(NO_3)_2 \cdot 4H_2O$ + $AgNO_3$ and $Cd(NO_3)_2 \cdot 4H_2O$ + $AgNO_3$ mixtures, at temperatures ranging between 293.2 and 363.2 K, are presented in Tables I and II. Equivalent volumes were calculated by using mass of the mixtures containing 1 mol of NO_3^- ions. Temperature dependence of density

Table I. Density Data of the Calcium Nitrate Tetrahydrate + Silver Nitrate System

	X_{Ag}				
T, K	0.055	0.104	0.148	0.188	0.225
293.2	1.7929	1.8354	1.8695	1.9180	
298.2	1.7875	1.8309	1.8645	1.9134	1.9475
303.2	1.7831	1.8266	1.8596	1.9084	1.9432
308.2	1.7781	1.8224	1.8546	1.9035	1.9380
313.2	1.7741	1.8169	1.8500	1.8986	1.9335
318.2	1.7696	1.8125	1.8445	1.8938	1.9285
323.2	1.7653	1.8081	1.8401	1.8891	1.9239
328.2	1.7608	1.8036	1.8360	1.8842	1.9190
333.2	1.7565	1.7993	1.8312	1.8795	1.9141
338.2	1.7523	1.7948	1.8266	1.8748	1.9093
343.2	1.7481	1.7905	1.8222	1.8701	1.9044
348.2	1.7440	1.7862	1.8173	1.8654	1.8995
353.2	1.7395	1.7819	1.8131	1.8608	1.8946
358.2	1.7352	1.7770	1.8086	1.8562	1.8897
363.2	1.7310	1.7732	1.8042	1.8512	1.8848

Table II. Density Data of the Cadmium Nitrate Tetrahydrate + Silver Nitrate System

	X_{Ag}					
T, K	0.064	0.121	0.167	0.222	0.308	0.354
293.2	2.3275	2.3595	2.3952			
298.2	2.3213	2.3534	2.3893	2.4319	2.5099	
303.2	2.3153	2.3474	2.3835	2.4259	2.5036	
308.2	2.3104	2.3415	2.3777	2.4199	2.4973	2.5412
313.2	2.3044	2.3354	2.3714	2.4140	2.4910	2.5358
318.2	2.2986	2.3297	2.3648	2.4081	2.4848	2.5296
323.2	2.2925	2.3235	2.3586	2.4014	2.4791	2.5229
328.2	2.2864	2.3174	2.3524	2.3956	2.4731	2.5168
333.2	2.2801	2.3114	2.3462	2.3894	2.4672	2.5108
338.2	2.2743	2.3054	2.3401	2.3831	2.4611	2.5039
343.2	2.2583	2.2990	2.3343	2.3769	2.4550	2.4978
348.2	2.2622	2.2930	2.3265	2.3708	2.4490	2.4914
353.2	2.2543	2.2871	2.3206	2.3650	2.4428	2.4852
353.2	2.2480	2.2810	2.3148	2.3591	2.4368	2.4790
363.2	2.2418	2.2750	2.3090	2.3528	2.4309	2.4730

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