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

Table III. Least-Squares Equations of Density and Equivalent Volume Data for Calcium and Cadmium Nitrate Tetrahydrate + Silver Nitrate Systems

equiv fraction X'_{Ag}	mole fraction X_{Ag}	temp range, K	data points	$\rho = A - B(T - 300)$, g cm^{-3}			$V_e = A' + B'(T - 300)$, cm^3 equiv^{-1}			
				A	10^3B	10^3SE[a]	A'	$10^2B'$	SE[a]	$10^4\alpha$, K^{-1}
				$Ca(NO_3)_2 \cdot 4H_2O + AgNO_3$						
0.028	0.055	290–365	15	1.785 83	0.873 40	0.43	66.928 62	3.365 96	0.011	4.92
0.055	0.104	290–365	15	1.829 06	0.884 60	0.31	66.086 08	3.336 61	0.018	4.92
0.080	0.148	290–365	15	1.864 23	0.902 61	0.26	65.592 93	3.339 95	0.008	4.96
0.104	0.188	290–365	15	1.911 33	0.953 02	0.13	64.583 88	3.348 16	0.007	5.04
0.125	0.225	300–365	13	1.946 13	0.967 62	0.17	64.028 66	3.387 40	0.011	5.35
				$Cd(NO_3)_2 \cdot 4H_2O + AgNO_3$						
0.032	0.064	290–365	13	2.315 35	1.188 54	0.36	66.703 06	3.496 76	0.013	5.20
0.064	0.121	290–365	13	2.351 40	1.206 45	0.17	66.014 05	3.463 78	0.006	5.21
0.091	0.167	290–365	11	2.387 27	1.233 89	0.31	65.197 37	3.438 16	0.010	5.25
0.125	0.222	295–365	11	2.429 80	1.218 59	0.21	64.274 87	3.291 69	0.008	5.10
0.185	0.308	305–365	10	2.507 11	1.229 00	0.23	62.654 58	3.114 92	0.011	4.95
0.215	0.354	325–365	88	2.552 77	1.265 56	0.23	61.726 12	3.169 47	0.006	5.05

[a] SE = standard error.

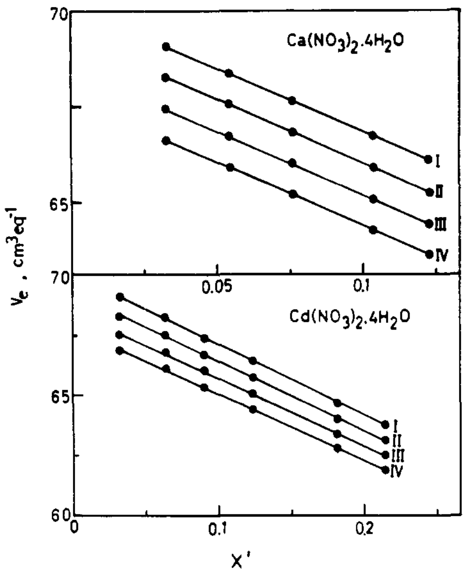

Figure 1. Equivalent volume (V_e) vs. equivalent fraction (X') isotherms for (Ca, Cd)$(NO_3)_2 \cdot 4H_2O + AgNO_3$ systems: I, 363.2 K; II, 343.2 K; III, 323.2 K; IV, 303.2 K.

(ρ) and equivalent volume (V_e) could be expressed by the equation of the type

$$\rho,\ V_e = A + B(T - 300) \qquad (1)$$

Coefficients A and B, characteristic of composition, and the standard errors are given in Table III. The mean expansion coefficients ($\alpha = (-1/\rho)(d\rho/dT)$) are almost constant (Table III), indicating absence of significant structural changes on addition of $AgNO_3$. The mean expansivity, B of V_e–T fittings, decreases with the addition of $AgNO_3$, indicating a decrease in van der Waal's volume of the system (cf. ref 19).

Equivalent volume (V_e) vs. equivalent fraction (X') isotherms (Figure 1) exhibit a decrease in V_e with an increase in silver nitrate content. This appears logical as larger hydrated cations $Ca(H_2O)_4^{2+}$ (radius = 3.75 Å) and $Cd(H_2O)_4^{2+}$ (radius = 3.77 Å) are gradually replaced by Ag^+ (radius = 1.26 Å) ions. The small deviations (less than 0.1%) from linearity in large scale V_e–X' plots suggest that on mixing of the solution, the volume of the system is determined by the additivity rule

$$V_e = X_1'\bar{V}_1 + X_2'\bar{V}_2 \qquad (2)$$

where X_i' and $\bar{V}_i$ are the equivalent fraction and the partial equivalent volume of the ith component. Partial equivalent volumes of the components (Table IV) were evaluated from

Table IV. Partial Equivalent Volumes of the Components of the $M(NO_3)_2 \cdot 4H_2O + AgNO_3$ Systems

T, K	$\bar{V}_{M(NO_3)_2 \cdot 4H_2O}$, cm^3 equiv^{-2}	$\bar{V}_{AgNO_3}$, cm^3 equiv^{-2}
	$Ca(NO_3)_2 \cdot 4H_2O + AgNO_3$	
303.2	67.84	40.02 (40.60)[a]
323.2	68.55	40.40
343.2	69.34	40.78
363.2	70.12	41.12
	$Cd(NO_3)_2 \cdot 4H_2O + AgNO_3$	
303.2	67.68	40.08 (39.03)[b]
323.2	68.50	40.44
343.2	69.38	40.76
363.2	70.19	41.10

[a] Extrapolated from molten salt data (*13*). [b] Volume of solid at 292.2 K.

V_e–X' isotherms by the graphical extrapolation method. Computed partial equivalent volumes of the hydrated salts may be compared with the measured volumes of the pure components (*1*, *4*, *15*, *18*, 19) and that of silver nitrate may be compared with the volumes extrapolated from molten salt data (*13*); in both cases the extrapolated and computed volumes are in good agreement. This also suggests that Ag^+ ions do not compete for water of hydration originally present in the coordination of divalent cations (*1*, *4*, *15*).

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Thermal Expansion and Shear Viscosity Coefficients of Water + Ethanol + Sucrose Mixtures

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Thermal expansion coefficients of water + ethanol + sucrose mixtures have been measured in the temperature range 10–60 °C, and shear viscosity coefficients have been measured in the temperature range 25–50 °C.

At ambient temperature the system water + ethanol exhibits large deviations from thermodynamic ideality—positive excess Gibbs free energies (*1*) and negative excess enthalpies (*2*) and volumes (*3*)—and anomalies in its viscosity (*4*). The extrema in the shear viscosity and excess enthalpy occur at an ethanol mass fraction of about 0.4. On the other hand, aqueous sucrose solutions are thermodynamically ideal, and the viscosity increases in a normal manner with increasing sucrose concentration (*5*).

We have studied the ternary system water (1) + ethanol (2) + sucrose (3) at mass fractions $w_2 \lesssim 0.3$ and $w_3 \lesssim 0.2$. Some preliminary solubility measurements at 25 °C established the solid–liquid phase diagram sketched in Figure 1. We report measurements at accessible liquid compositions at essentially 1 atm pressure of (i) the thermal expansion coefficient α_p in the range 10–60 °C and (ii) the shear viscosity coefficient η in the range 25–50 °C.

Experimental Section

Materials. The ethanol used in the dilatometry measurements and some of the viscometry measurements was AnalaR grade (British Drug Houses Ltd.); in the remaining viscometry measurements an allowance was made for a trace of water in the ethanol (<0.5%). The tap water was freshly distilled, and sucrose was a commercial sample from the British Sugar Corp.

Solutions were degassed under vacuum before use. Air solubility in water + ethanol is anomalously low (*6*), and a separate program of excess volume experiments by dilution dilatometry (*7*) had to be abandoned owing to the formation of air bubbles (despite careful degassing) on mixing ethanol with an aqueous sucrose solution.

Apparatus. The dilatometers were of the design described by Orwoll and Flory (*8*). Changes in sample volume were obtained by weighing the amounts of displaced mercury. Temperatures were measured with a Hewlett-Packard quartz-crystal thermometer in a water thermostat bath (≲318 K, ±2 mK; ≳318 K, ±3 mK). Appropriate corrections were made for the thermal expansion of glass and mercury (*8*).

Viscosities were measured with two Ubbelohde suspended-level viscometers (*9*). The manufacturer's calibrations were checked by measurements on distilled water from 25 to 50 °C. The passage of the meniscus was detected photoelectrically, with infrared emitters and detectors connected to the viscometer by flexible light cables (*10*). The mean flow-time was an average of five determinations. A small kinetic energy correction was applied. Shear viscosities were calculated from the measured kinematic viscosities and the densities obtained in the dilatometric work.

Table I. Thermal Expansion Coefficients for Mixtures Made from 8.31% Aqueous Ethanol

	$10^3\alpha_p/K^{-1}$ sucrose mass fraction			
t/°C	0	0.0491	0.0964	0.1859
9.82	0.126	0.156	0.182	0.230
13.23	0.168	0.195	0.217	0.258
16.94	0.213	0.236	0.254	0.288
19.27	0.237	0.260	0.276	0.309
21.74	0.264	0.284	0.299	0.325
24.22	0.289	0.308	0.319	0.342
26.53	0.312	0.328	0.340	0.361
29.31	0.339	0.355	0.363	0.381
32.75	0.369	0.382	0.388	0.403
36.12	0.399	0.410	0.416	0.424
38.51	0.419	0.428	0.433	0.441
40.98	0.439	0.447	0.450	0.456
44.08	0.466	0.473	0.473	0.477
46.53	0.479	0.486	0.486	0.487
48.41	0.497	0.503	0.500	0.501
50.13	0.504	0.509	0.509	0.504
52.13	0.526	0.531	0.527	0.523
54.73	0.543	0.546	0.541	0.537
57.56	0.562	0.564	0.558	0.551
60.28	0.576	0.579	0.573	0.566

Results of Measurements

Tables I and II list isobaric thermal expansion coefficients $\alpha_p = (\partial \ln V/\partial T)_p$ from 10 to 60 °C for eight mixtures. The results in Table I are for solutions made up from a water + ethanol mixture of ethanol mass fraction $w_2 = 0.0831$ by dissolving various mass fractions w_3 of sucrose (0, 0.0491, 0.0964, and 0.1859) in the mixed solvent. (The w_2 values, therefore, do not represent the mass fractions of ethanol in the final mixture.) The results in Table II are for solutions made up from water + ethanol with $w_2 = 0.1629$. The precision of the α_p values is about 0.5%. Densities at 20.0 °C are listed in Table III, and for $w_3 = 0$ they agree with Osborn (*3*) within 0.01%.

Shear viscosity coefficients η for 15 mixtures from 25 to 50 °C are recorded in Table IV. Three different mass fractions of sucrose have been studied (0.0476, 0.0909, and 0.1667). The accuracy of the η values is estimated to be about 1%. Results

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