Li^+ show a tendency to remove water from the hydration sheath of divalent cations.

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Received for review June 28, 1978. Accepted March 12, 1979. Authors thank the University Grants Commission, and the Council of Scientific and Industrial Research, for financial assistance and a junior research fellowship (to K.B.).

Supplementary Material Available: Density data of molten $Zn(NO_3)_2 \cdot 6.02H_2O + MNO_3$ systems (3 pages). Ordering information is given on any current masthead page.

Volumetric Properties of Molten Hydrated Salts. 3. Calcium and Cadmium Nitrate Tetrahydrate with Thallium(I) Nitrate

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Densities of molten calcium and cadmium nitrate tetrahydrates with thallium(I) nitrate were measured by using a manometric densitometer. Temperature dependence of density and equivalent volume was found to be linear. Composition variation of volumes obeys the principle of additivity of volumes and suggests that water of hydration remains with divalent cations.

The concentrated solutions of dipositive cations containing 4–6 mol of water/mol of cation confer essentially the same properties as expected from the "hard sphere" cations of some charge/radius ratio (*1*). These systems are of intrinsic chemical and possibly future applied interest because of their low liquidus temperature, good solvent properties, high conductivity, and supercooling and glass-forming tendencies (*1–3*). In continuation to our studies of these systems (*6–9*) results of density measurements on $Ca(NO_3)_2 \cdot 4H_2O + TlNO_3$ and $Cd(NO_3)_2 \cdot 4H_2O + TlNO_3$ mixtures are presented here.

Experimental Section

Calcium and cadmium nitrate tetrahydrates were AnalaR (BDH) grade; the water content of the salts, determined by volumetric titration by using EDTA, was within ±0.01 of the stoichiometric value. Thallium(I) nitrate, extra pure (VEB Laboratories), was dried to constant mass at 150 °C and stored over anhydrous magnesium perchlorate until used.

A manometric densitometer (*6*) was used to measure the volume of a known amount of melt. Details of the experiments, calibration and precision in the acquisition of data, etc., have been described earlier (*6*). Data were obtained in both heating and cooling cycles at 5 K intervals.

Results and Discussion

The densities of $Ca(NO_3)_2 \cdot 4H_2O + TlNO_3$ and $Cd(NO_3)_2 \cdot 4H_2O + TlNO_3$ mixtures containing up to 22.5 and 27.5 mol % of $TlNO_3$, respectively, were obtained at temperatures ranging between 288.2 and 363.2 K and presented in Tables I and II.

Table I. Density (g cm^{-1}) Data of the Calcium Nitrate Tetrahydrate + Thallium(I) Nitrate System

	x_{Tl}			
T, K	0.037	0.074	0.153	0.226
293.2	1.8072	1.8602	1.9823	2.1093
298.2	1.8025	1.8556	1.9778	2.1047
303.2	1.7979	1.8509	1.9732	2.1002
308.2	1.7933	1.8462	1.9687	2.0957
313.2	1.7886	1.8416	1.9641	2.0914
318.2	1.7840	1.8372	1.9596	2.0864
323.2	1.7794	1.8325	1.9550	2.0820
328.2	1.7748	1.8279	1.9505	2.0775
333.2	1.7702	1.8234	1.9459	2.0730
338.2	1.7655	1.8188	1.9414	2.0686
343.2	1.7610	1.8142	1.9368	2.0643
348.2	1.7564	1.8096	1.9323	2.0593
353.2	1.7517	1.8048	1.9277	2.0552
358.2	1.7470	1.8002	1.9232	2.0507
363.2	1.7424	1.7957	1.9186	2.0464

Table II. Density (g cm^{-3}) Data of the Cadmium Nitrate Tetrahydrate + Thallium(I) Nitrate System

	x_{Tl}				
T, K	0.042	0.086	0.161	0.223	0.277
293.2	2.3243	2.3798	2.4812	2.5751	2.6627
298.2	2.3186	2.3742	2.4755	2.5695	2.6571
303.2	2.3128	2.3685	2.4698	2.5637	2.6516
308.2	2.3071	2.3629	2.4642	2.5582	2.6460
313.2	2.3013	2.3572	2.4587	2.5526	2.6404
318.2	2.2956	2.3516	2.4532	2.5470	2.6349
323.2	2.2898	2.3459	2.4475	2.5414	2.6293
328.2	2.2841	2.3403	2.4419	2.5358	2.6237
333.2	2.2783	2.3346	2.4363	2.5301	2.6182
338.2	2.2726	2.3290	2.4307	2.5245	2.6126
343.2	2.2668	2.3233	2.4250	2.5189	2.6070
348.2	2.2611	2.3176	2.4194	2.5133	2.6014
353.2	2.2553	2.3120	2.4138	2.5077	2.5958
358.2	2.2496	2.3064	2.4082	2.5020	2.5902
363.2	2.2438	2.3007	2.4026	2.4964	2.5847

Equivalent volumes were calculated by using the mass of the mixture containing 1 g-mol of NO_3^- ions. Temperature-dependence of density (ρ) and equivalent volume (V_e) was found

0021-9568/79/1724-0185$01.00/0

Table III. Least-Squares Equation of Density and Equivalent Volume Data for Calcium and Cadmium Nitrate Tetrahydrate + Thallium(I) Nitrate Systems

equiv fraction (X_{Tl}')	mol fraction (X_{Tl})	T, K	data points	$\rho = A - B(T - 300)$, g cm^{-3}			$V_e = A' + B'(T - 300)$, cm^3 equiv^{-1}			$10^4\alpha$, K^{-1}
				A	10^3B	10^3SE[a]	A'	$10^2B'$	SE[a]	
				$Ca(NO_3)_2{\cdot}4H_2O + TlNO_3$						
0.019	0.037	290-365	15	1.800 85	0.924 29	0.05	67.120 13	3.551 85	0.009	5.21
0.039	0.073	290-365	15	1.853 87	0.920 53	0.09	66.769 31	3.403 87	0.010	5.04
0.083	0.153	290-365	15	1.976 12	0.909 89	0.03	65.949 09	3.116 13	0.007	4.67
0.127	0.226	290-365	15	2.103 02	0.899 48	0.15	65.117 30	2.853 15	0.006	4.33
				$Cd(NO_3)_2{\cdot}4H_2O + TlNO_3$						
0.021	0.042	290-365	15	2.316 49	1.149 89	0.03	67.611 71	3.449 71	0.010	5.04
0.045	0.085	290-365	15	2.372 13	1.129 76	0.03	67.141 68	3.284 47	0.007	4.83
0.087	0.161	290-365	15	2.473 49	1.121 58	0.06	66.307 40	3.091 14	0.007	4.60
0.126	0.223	290-365	15	2.567 42	1.123 37	0.05	65.558 58	2.938 22	0.008	4.43
0.160	0.277	290-365	15	2.655 13	1.114 62	0.04	64.880 65	2.788 93	0.007	4.25

[a] SE = standard error.

Table IV. Partial Equivalent Volumes-Temperature Equations for $M(NO_3)_2{\cdot}4H_2O + TlNO_3$ Systems

system	$\bar{V}_{M(NO_3)_2{\cdot}4H_2O}$, cm^3 equiv^{-2}	$\bar{V}_{TlNO_3}$, cm^3 equiv^{-2}	vol of $TlNO_3$ at 363.2 K, cm^3 equiv^{-1}
$Ca(NO_3)_2{\cdot}4H_2O + TlNO_3$	$67.44 + 3.75 \times 10^{-2}\,(T - 300)$	$46.59 + 2.38 \times 10^{-2}\,(T - 300)$	48.00 (51.91)[a]
$Cd(NO_3)_2{\cdot}4H_2O + TlNO_3$	$68.00 + 3.60 \times 10^{-2}\,(T - 300)$	$47.13 + 2.60 \times 10^{-2}\,(T - 300)$	48.76 (47.94)[b]

[a] From ref 4. [b] Volume of solid at 294.6 K.

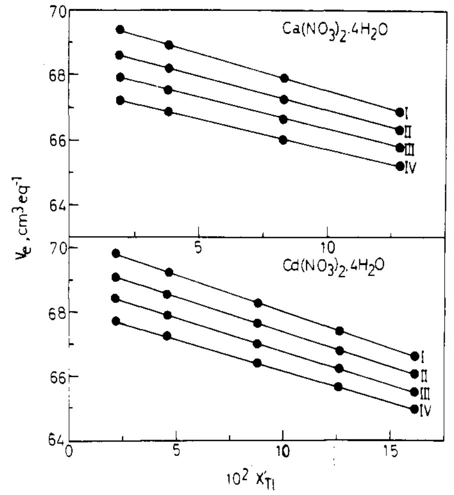

Figure 1. Equivalent volume (V_e) vs. equivalent fraction (X') isotherms for $(Ca, Cd)(NO_3)_2{\cdot}4H_2O + TlNO_3$ systems: I, 363.2 K; II, 343.2 K; III, 323.2 K; IV, 303.2 K.

to be linear. The data were least-squares fitted into an equation of the type

$$\rho, V_e = A \pm B(T - 300)$$

by using an IBM 360/44 data processing system. The coefficients A and B and the standard errors are included in Table III. The mean expansion coefficients $\alpha = -(1/\rho)(d\rho/dT)$ of the mixtures (Table III) exhibit a decreasing trend on addition of $TlNO_3$. The mean expansivity (B of V_e–T fittings) of the system also decreases with increase in $TlNO_3$ content indicating a decrease in van der Waals volume of the system (*7*).

Equivalent volume (V_e)-equivalent fraction (X') isotherms (Figure 1) exhibit a decrease in V_e with increase in thallium(I) nitrate content; this appears logical as the larger hydrated cations $Ca(H_2O)_4^{2+}$ (3.75 Å) and $Cd(H_2O)_4^{2+}$ (3.77 Å) are gradually replaced by Tl^+ (1.47 Å) ions. Large scale plots (not shown) showed that for V_e–X' plots, deviations from linearity were less than 0.1%, so that volumetrically the systems may be considered as ideal in the composition range studied. Partial equivalent volumes, evaluated from V_e–X' isotherms by graphical extrapolation and also by least-squares fitting of V_e–X' data into a linear equation, are given in Table IV. Computed partial equivalent volumes of hydrated salts may be compared with the measured volumes of the pure components (*1*, *2*, *3*, *5*) and those of thallium(I) nitrate with the volumes extrapolated from molten salt data (*4*); in both cases the extrapolated and computed values are in good agreement. The additivity of volumes and the close agreement between computed and extrapolated partial equivalent volumes of the components suggest that Tl^+ ions do not compete for water of hydration originally present in the coordination of divalent cations (*1*, *2*).

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Received for review November 27, 1978. Accepted March 12, 1979. The authors thank the University Grants Commission, New Delhi, for financial assistance to the project, "Thermodynamics and Electrochemistry of Molten Salts", and a senior research fellowship (to RCS).