various mixtures thus obtained are given in Table III at 30 and 40 °C.

It may be noted from Table III that except for the dimethyl sulfoxide + nitrobenzene system, all other mixtures have negative excess surface tensions at all concentrations, i.e., $\gamma^E < 0$. The negative excess volume of mixing values, i.e., $V_m^E < 0$ have already been reported by us (*3*). These results would suggest the presence of specific interactions in all these mixtures. A somewhat similar type of conclusion was drawn by Nigam and Dhillon (*7*) for some binary mixtures.

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Volumetric Properties of Molten Hydrated Salts. 2. Zinc Nitrate Hexahydrate + Alkali Metal Nitrates

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Densities of molten $Zn(NO_3)_2 \cdot 6H_2O$ + MNO_3 (M = Li, Na, K, Rb, Cs) systems have been measured by using a manometric densitometer at temperatures ranging between 288.2 and 363.2 K. Temperature dependence of densities and equivalent volumes was found to be linear. Equivalent volumes of all systems except those containing lithium nitrate were additive; small positive deviations in the latter have been considered to arise due to preferential hydration of Li^+ ions.

Mass and transport behavior of molten hydrated salts containing 4–6 mol of water/mol of the electrolyte have been explained (*1–7*, *9–14*, *17*, *18*) by assuming that the water of hydration is almost wholly associated with the cation, forming weak field species of the type $M(H_2O)_n^{2+}$. They have low liquidus temperature, and some of their solutions in the presence of alkali metal ions show appreciable tendency to supercool. In view of the recent interest in them and in continuation of our studies on these systems (*3*, *17*, *18*), the densities of molten $Zn(NO_3)_2 \cdot 6H_2O$ + MNO_3 systems, where M = Li, Na, K, Rb, and Cs, are presented in this paper.

Experimental Section

An approximately 5-kg batch of hydrated zinc nitrate, LR (BDH) grade, was melted and filtered through a sintered glass tube (porosity G-3) into several airtight bottles. Water content of a sample, determined by volumetric titration by using EDTA, was found to be 6.02 ± 0.01 mol/mol of zinc nitrate. The alkali metal nitrates, AnalaR (BDH) or equivalent purity, were desiccated to constant mass at 400–450 K. Calculated amounts of these were added to bottles containing hydrated zinc nitrate which were matured at about 40 °C for about 1 h before use; loss of water content during this was found to be negligible.

The densitometer, experimental details of measurements, and the precision attained have been discussed earlier (*16*).

Results and Discussion

Density (ρ) data of $Zn(NO_3)_2 \cdot 6H_2O$ + MNO_3 (M = Li, Na, K, Rb, Cs) mixtures were obtained at an interval of 5 K in the temperature range 288.2–363.2 K. Equivalent volumes (V_e) were calculated by using the mass of mixture containing 1 mol of NO_3^- ions (cf. *15*, *17*, *18*). Variation of ρ and V_e with temperature was found to be linear; data were least-squares fitted into an equation of type

$$(\rho . V_e) = A \pm B(T - 300) \qquad (1)$$

Coefficients A and B which were characteristic of the composition are given in Table I. Almost constant values of expansion coefficients ($\alpha = -(1/\rho)(d\rho/dT)$) over the measured concentration range employed and with the different cations indicate absence of any significant structural changes on addition of the alkali metal nitrates. A smooth change in "mean equivalent expansivity" (coefficient B of V_e–T equation) also supports this.

Equivalent volume (V_e) vs. equivalent fraction (X') isotherms of the $Zn(NO_3)_2 \cdot 6H_2O$ + $LiNO_3$ system (Figure 1) exhibit a small positive deviation (2–5%) in large scale plots (not shown) indicating a decrease in packing density on addition of $LiNO_3$. Li^+ ions having high charge density and greater hydrophilic tendency relative to $Zn(H_2O)_6^{2+}$ ions will probably dehydrate the latter by a displacement reaction of the type

$$Zn(H_2O)_6^{2+} + Li^+ \rightarrow Zn(H_2O)_{6-x}^{2+} + Li(H_2O)_x^+$$

The resultant increased size of (hydrated) Li^+ ions will decrease the packing density of the system. The computed and extrapolated partial equivalent volumes of $LiNO_3$ (taking linear V_e–X'

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Table I. Least-Squares Equations of Density and Equivalent Volume Data for the $Zn(NO_3)_2\cdot 6H_2O + MNO_3$ System

			$\rho = A - B(T - 300)$, g cm^{-3}			$V_e = A' + B'(T - 300)$, cm^3			
X_{MNO_3}	T, K	data points	A	10^3B	10^3SE^a	A'	$10^2B'$	SE^a	$10^4\alpha$
				$MNO_3 = LiNO_3$					
0.0000	290-365	13	1.8629	1.1736	0.12	79.8218	5.2494	0.015	6.4
0.0852	290-365	15	1.8386	1.1666	0.15	78.9479	5.1736	0.004	6.5
0.2013	290-365	15	1.8350	1.1660	0.28	76.1749	4.9833	0.016	6.5
0.3498	290-365	15	1.8400	1.1735	0.23	71.6267	4.7107	0.004	6.5
0.4689	290-365	15	1.8466	1.1789	0.13	67.2945	4.4460	0.004	6.5
				$MNO_3 = NaNO_3$					
0.0506	298-363	27	1.8271	1.0883	0.05	80.4824	4.9749	0.032	6.1
0.0727	298-363	27	1.8330	1.0775	0.02	79.8163	4.8549	0.011	6.0
0.1227	298-363	27	1.8447	1.1119	0.05	78.3541	4.9014	0.024	6.1
0.1507	298-363	27	1.8450	1.0628	0.03	77.8363	4.6413	0.009	5.9
0.2026	298-363	27	1.8506	1.1311	0.05	76.4728	4.8546	0.029	6.2
				$MNO_3 = KNO_3$					
0.0512	298-353	24	1.8388	1.0757	0.02	80.1943	4.8386	0.014	5.9
0.1210	298-353	24	1.8469	1.1124	0.08	78.8587	4.9569	0.042	6.2
0.1899	298-353	24	1.8628	1.1161	0.04	77.1500	4.9677	0.019	6.3
0.2608	298-353	24	1.8750	1.1158	0.04	75.5021	4.8183	0.019	6.3
0.3115	298-353	24	1.8825	1.1020	0.03	74.3292	4.4942	0.012	6.0
0.3999	298-353	24	1.8977	1.1428	0.02	72.0951	4.4829	0.015	6.1
				$MNO_3 = RbNO_3$					
0.0510	298-358	22	1.8377	1.0823	0.06	80.8995	4.9409	0.033	6.0
0.1015	298-358	22	1.8521	1.0597	0.09	80.2496	4.7636	0.034	5.8
0.1506	298-358	23	1.8742	1.0858	0.03	79.2936	4.7459	0.017	5.9
0.1944	298-363	27	1.8971	1.0946	0.06	78.3168	4.6780	0.030	5.9
0.3009	298-363	27	1.8671	1.1573	0.08	77.8348	4.8962	0.029	6.0
0.4004	293-363	29	2.0029	1.1869	0.04	74.0928	4.5413	0.024	6.0
0.4678	293-363	29	2.0533	1.2986	0.03	72.2369	4.7430	0.012	6.5
				$MNO_3 = CsNO_3$					
0.0296	285-365	16	1.8494	1.1752	0.04	80.7854	5.2823	0.020	6.5
0.0709	285-365	16	1.8765	1.1658	0.02	80.1586	5.1111	0.015	6.3
0.1324	290-365	15	1.9169	1.2277	0.01	79.2881	5.2326	0.005	6.5
0.2339	290-365	15	1.9841	1.2535	0.02	78.0282	5.0976	0.009	6.5

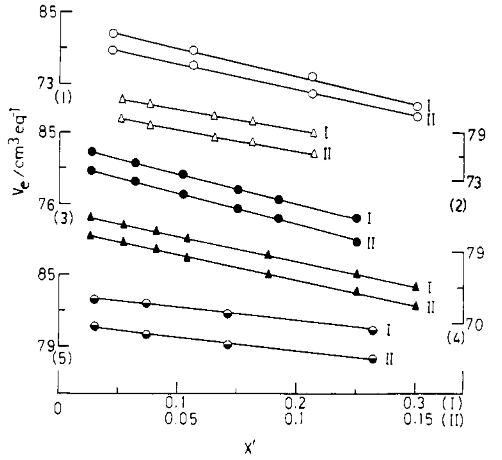

Figure 1. Equivalent volume (V_e) vs. equivalent fraction (X') isotherms of $Zn(NO_3)_2\cdot 6H_2O + MNO_3$ (M = O, Li; △, Na; ●, K; ▲, Rb; ⊖, Cs) systems. Temperature for I is 348.2 and II is 298.2 K. Scale on x axis is (I) for Li, K, and Rb and (II) for Na and Cs. Scale on y axis is (1) Li, (2) Na, (3) K, (4) Rb, and (5) Cs.

plots, Table II) also differ by 5% indicating that the principle of additivity of volumes is not applicable to this system.

V_e vs. X' isotherms exhibit a decrease in V_e with increase in X' for $Zn(NO_3)_2\cdot 6H_2O + MNO_3$ (M = Na, K, Rb, Cs) systems (also Figure 1) which is in accordance with the fact that larger hydrated cations, $Zn(H_2O)_6^{2+}$ (r = 3.52 Å) are replaced by smaller alkali metal cations Na^+ (r = 0.98 Å), K^+ (r = 1.33 Å), Rb^+ (r = 1.43 Å), Cs^+ (r = 1.63 Å), in "per equivalent" unit. (The radius of hydrated zinc ions ($Zn(H_2O)_6^{2+}$) is taken equal to the sum of radii of the Zn^{2+} ion and twice of the H_2O molecule ($r_{Zn^{2+}} + 2r_{H_2O}$).) The linearity of V_e vs. X' plots indicates that these systems are volumetrically ideal; the partial equivalent volumes being independent of composition and equal to the equivalent volumes of the pure components at the corresponding temperature. Partial equivalent volumes ($\bar{V}_i$), evaluated by the graphical extrapolation method, are given in Table II. The computed partial equivalent volumes of $Zn(NO_3)_2\cdot 6H_2O$ may be compared with the measured volumes of pure component (*12*) and those of alkali metal nitrates with the volumes extrapolated from molten salt data (*8*); the two values are in reasonable agreement providing support to the principle of additivity of volumes. It may also be concluded that Na^+, K^+, Rb^+, and Cs^+ ions do not compete for water of hydration originally present in the coordination of divalent cation (*1*, *2*, *4*, *17*, *18*).

Table II. Partial Equivalent Volumes ($\bar{V}_i$) of the Components of $Zn(NO_3)_2\cdot 6H_2O + MNO_3$ Systems

MNO_3	temp, K	$\bar{V}_{Zn(NO_3)_2\cdot 6H_2O}$, cm^3 equiv^{-2}	$\bar{V}_{MNO_3}$, cm^3 equiv^{-2}
$LiNO_3$	298.2	80.95	35.71
	323.2	82.12 (82.05)^a	37.08 (35.48)^b
	348.2	83.40	38.76
$NaNO_3$	298.2	81.45	38.76
	323.2	82.55	39.75 (40.74)^b
	348.2	83.75	40.95
KNO_3	298.2	81.00	47.39
	323.2	82.12	48.07 (48.64)^b
	348.2	83.45	49.40
$RbNO_3$	298.2	81.56	51.46
	323.2	82.70	52.53 (52.83)^b
	348.2	83.95	53.48
$CsNO_3$	298.2	81.07	56.16
	323.2	82.30	58.29 (58.23)^b
	348.2	83.37	60.46

^{a} From ref 12. ^{b} Calculated from molten salt data of ref 8.

Though the principle of additivity of volumes is a good approximation to evaluate the volumes of the mixtures from limited data, it is not valid where hydration-dehydration or other chemical or structural changes occur on mixing. Also, small cations like

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

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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

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