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Density and Partial Equivalent Volumes of Hydrated Melts: Tetrahydrates of Calcium Nitrate, Cadmium Nitrate, and Their Mixtures with Lithium, Sodium, and Potassium Nitrate

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Densities of $Ca(NO_3)_2 \cdot 4H_2O$–(Li, Na)NO_3 and $Cd(NO_3)_2 \cdot 4H_2O$–(Li, Na, K)NO_3 mixtures, as a function of temperature and alkali metal nitrate content, were determined by measuring the volume of a certain amount of melt in a precalibrated densitometer. For any pair of salts, the isotherms of equivalent volume vs. equivalent fraction of the monovalent ion were linear. The partial equivalent volume ($\bar{V}_{equiv}$) of the constituents was independent of the nature and composition of the melt at a given temperature.

The studies of concentrated aqueous electrolytes are of great importance in understanding the behavior of molten salts (*1–6*). Angell (*1–3*) postulated the existence of hydrated divalent cations in hydrated melts of calcium and magnesium nitrate and emphasized that these melts could be considered as analogs of molten salts.

Braunstein et al. (*6*), during their investigations on various aspects of some aqueous nitrate melts, measured the densities of calcium nitrate tetrahydrate–potassium nitrate mixtures at 100°C and found that the assumption of additivity in strongly concentrated aqueous solutions may be a useful approximation. This study is aimed to explore, if the additivity of equivalent volumes can be regarded as a general characteristic of hydrated melts, particularly for the mixtures containing smaller monovalent cations, e.g., lithium and sodium ions.

Experimental

Material. $LiNO_3$, $NaNO_3$, KNO_3, $Ca(NO_3) \cdot 4H_2O$ (BDH), and $Cd(NO_3) \cdot 4H_2O$ (Reanal, Hungary) of analar grade were used without further purification. (An analytical cross check for the water content was done volumetrically by use of EDTA. The results established the composition of the tetrahydrates within ±0.01 to the stoichiometric composition.) Mixtures of varying compositions were prepared separately by melting the requisite amounts of the components in a sealed glass vessel and digesting them at 60–70°C for about 6 hr.

Apparatus and procedure. The manometric densitometer used by Husband (*8*) and Cleaver et al. (*7*) was modified to allow a direct measurement of the volume of a known amount of the melt. The volume capacity of the bulb was indicated by fixed fiducial marks on both limbs and was determined at room temperature with distilled water. No correction was made for the thermal expansion of the densitometer at higher temperatures. During measurements the meniscus of the liquid in the shorter limb was kept at a fixed mark by applying pressure from a manometer, and the expansion was read on the longer capillary (calibrated to 0.01 ml). A liquid paraffin bath (10 liters) was used as constant temperature bath. The temperature was controlled and measured with a precision better than ±0.1°C.

Results and Discussion

Densities of the various mixtures tabulated in Tables I and II varied linearly with temperature and were expressed by the equation

$$\rho = a - bt\ (^\circ C)$$

The linear density–temperature equations for the various mixtures investigated are presented in Tables III and IV.

Table I. Densities of $Ca(NO_3)_2 \cdot 4H_2O$–MNO_3 Mixtures

X'_{MNO_3}	Temp, °C	Density, g/cm³
	$Ca(NO_3)_2 \cdot 4H_2O$–$LiNO_3$	
0.0	14.5	1.7556
	23.0	1.7470
	34.3	1.7395
	39.9	1.7346
	49.2	1.7273
	60.2	1.7187
	69.2	1.7119
	79.3	1.7025
	83.7	1.6986

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Table I. Continued

X'_{MNO_3}	Temp, °C	Density, g/cm³
	$Ca(NO_3)_2 \cdot 4H_2O$-$LiNO_3$	
0.099	8.2	1.7721
	15.4	1.7645
	33.8	1.7495
	44.2	1.7413
	51.6	1.7358
	60.2	1.7280
	80.8	1.7113
0.147	5.9	1.7702
	15.0	1.7624
	25.7	1.7534
	42.8	1.7399
	51.2	1.7337
	58.6	1.7275
	65.8	1.7219
	75.6	1.7138
	81.5	1.7086
0.232	5.1	1.7857
	16.0	1.7767
	24.8	1.7695
	35.5	1.7606
	43.2	1.7547
	59.0	1.7420
	70.8	1.7327
	82.1	1.7223
0.305	10.7	1.7878
	17.8	1.7818
	27.2	1.7737
	36.4	1.7660
	43.3	1.7608
	54.4	1.7423
	61.4	1.7347
	70.3	1.7275
	80.0	1.7198
	$Ca(NO_3)_2 \cdot 4H_2O$-$NaNO_3$	
0.05	19.3	1.7563
	30.6	1.7461
	40.8	1.7383
	49.7	1.7311
	55.9	1.7265
	63.6	1.7197
	70.2	1.7143
	79.0	1.7067
0.08	10.8	1.7804
	14.2	1.7766
	19.2	1.7721
	30.1	1.7625
	39.6	1.7549
	47.4	1.7488
	54.4	1.7430
	60.9	1.7384
	68.1	1.7319
	73.2	1.7280
	78.0	1.7238
0.111	20.2	1.7762
	29.9	1.7670
	43.1	1.7564
	59.3	1.7433
	71.0	1.7340
	76.4	1.7291
	85.4	1.7203
0.143	50.0	1.8012
	53.3	1.7984
	57.0	1.7957
	59.9	1.7933
	64.7	1.7395
	74.6	1.7810
	78.0	1.7779

None of the experimental points deviated from straight line by more than 0.2%. Present results on the densities of calcium nitrate tetrahydrate, $\zeta = 1.7668 - 0.804 \times 10^{-3}\ t$, show good agreement with those reported by Moynihan (*10*), $\zeta = 1.768 - 0.85 \times 10^{-3}\ t$. Extrapolation of the present results to 100°C leads to a value of 1.686 g/cm³, which compares well with the value of 1.688 g/cm³ obtained by Braunstein et al. (*6*).

Isotherms of equivalent volume (V_{equiv}) vs. equivalent fraction (X') of the monovalent nitrate in the mixture were linear over the composition range studied. Partial equivalent volumes ($\bar{V}_{equiv}$) were computed by extrapolating these linear plots. Table V records the equations representing the temperature dependence of partial equivalent volumes of the constituents of each mixture. The average $\bar{V}_{equiv}$ at 75°C for $LiNO_3$, $NaNO_3$, KNO_3 obtained in these studies agree favorably (Table VI) with the values obtained by extrapolating the values of equivalent volumes (computed from literature density data (*9*) of these salts from the temperature of measurements to 75°C (a hypothetical supercooled state). This reflects

Table II. Densities of $Cd(NO_3)_2 \cdot 4H_2O$-MNO_3 Mixtures

X'_{MNO_3}	Temp, °C	Density, g/cm³
	$Cd(NO_3)_2 \cdot 4H_2O$-$LiNO_3$	
0.0	42.9	2.3017
	49.0	2.2955
	53.6	2.2905
	58.6	2.2836
	66.9	2.2747
	74.8	2.2684
	82.4	2.2588
	90.2	2.2502
0.095	47.4	2.2590
	57.9	2.2457
	65.3	2.2365
	67.8	2.2335
	69.6	2.2311
	77.3	2.2226
	83.5	2.2158
	91.2	2.2072
0.355	71.8	2.1609
	77.2	2.1549
	82.4	2.1489
	91.1	2.1393
	$Cd(NO_3)_2 \cdot 4H_2O$-$NaNO_3$	
0.081	48.9	2.2669
	56.5	2.2567
	65.3	2.2462
	77.5	2.2322
	90.0	2.2168
0.143	57.3	2.2583
	66.3	2.2478
	80.5	2.2316
	90.0	2.2206
	$Cd(NO_3)_2 \cdot 4H_2O$-KNO_3	
0.112	42.9	2.2765
	49.0	2.2698
	53.6	2.2646
	58.6	2.2585
	66.9	2.2495
	74.8	2.2400
	82.4	2.2307
	90.2	2.2226
0.392	47.4	2.2503
	59.7	2.2370
	86.1	2.2050
	94.0	2.1963

Table III. Density Equations for $Ca(NO_3)_2 \cdot 4H_2O$-(Li, Na)NO_3

Equiv of MNO_3	Temp, °C	$\rho = a - bt$ (g/cc) a	b	SE
			$LiNO_3$	
0.0	14.5–84	1.7668	0.804×10^{-3}	0.63×10^{-3}
0.099	8–81	1.7780	0.829	0.52
0.147	6–81	1.7746	0.805	0.30
0.232	5–82	1.7898	0.814	0.34
0.305	11–80	1.8009	1.031	2.37
			$NaNO_3$	
0.053	19–79	1.7719	0.821	0.33
0.081	11–78	1.7883	0.827	0.51
0.111	20–85	1.7927	0.838	0.54
0.143	50–78	1.8428	0.829	0.18

Table IV. Density Equations for $Cd(NO_3)_2 \cdot 4H_2O$-(Li, Na, K)NO_3

Equiv of MNO_3	Temp, °C	$\rho = a - bt$ (g/cc) a	b	SE
			$LiNO_3$	
0.0	43–90	2.3479	1.08×10^{-3}	0.68×10^{-3}
0.095	47–91	2.3138	1.18	0.58
0.355	71–91	2.2412	1.12	0.08
			$NaNO_3$	
0.081	49–90	2.3253	1.20	0.40
0.143	57–80	2.3241	1.15	0.08
			KNO_3	
0.112	43–90	2.3260	1.15	0.28
0.392	47–94	2.3063	1.17	0.45

Table V. Partial Equivalent Volumes for One Equivalent of NO_3^-

System	$\bar{V}_{M'(NO_3)_2 \cdot 4H_2O}$	$\bar{V}_{MNO_3}$
$Ca(NO_3)_2 \cdot 4H_2O$-$LiNO_3$	$69.11 + 3.2 \times 10^{-2} (t - 75)$	$38.15 + 3.5 \times 10^{-2} (t - 75)$
$Ca(NO_3)_2 \cdot 4H_2O$-$NaNO_3$	$69.23 + 3.2 \times 10^{-2} (t - 75)$	$41.04 + 2.6 \times 10^{-2} (t - 75)$
$Cd(NO_3)_2 \cdot 4H_2O$-$LiNO_3$	$68.25 + 3.4 \times 10^{-2} (t - 75)$	$38.06 + 2.5 \times 10^{-2} (t - 75)$
$Cd(NO_3)_2 \cdot 4H_2O$-$NaNO_3$	$68.18 + 3.3 \times 10^{-2} (t - 75)$	$43.75 + 4.0 \times 10^{-2} (t - 75)$
$Cd(NO_3)_2 \cdot 4H_2O$-KNO_3	$68.23 + 3.3 \times 10^{-2} (t - 75)$	$47.79 + 3.0 \times 10^{-2} (t - 75)$

Table VI. Comparison of $\bar{V}_{equiv}$ with Extrapolated Values

Salt	$\bar{V}_{equiv}$, av	$\bar{V}_{equiv}$, extrapolated
$LiNO_3$	38.11	36.74
$NaNO_3$	42.40	41.04
KNO_3	47.79	49.00
$Ca(NO_3)_2 \cdot 4H_2O$	69.17	...
$Cd(NO_3)_2 \cdot 4H_2O$	69.22	...

that the additivity of equivalent volumes in hydrated melts could be regarded a general characteristic of these systems. However, the discrepancy in $LiNO_3$ appears to be significant because of the smaller liquid state extrapolation.

The additivity of volumes and the fact that the $\bar{V}_{equiv}$ of $Ca(NO_3)_2 \cdot 4H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ are insensitive to the nature of the "foreign" ion present in the mixture suggest that in the mixtures containing smaller monovalent ions, e.g., Li^+, the water remains preferentially attached to divalent ions, or the changes in hydration occur systematically with composition change in such a way that the volume-composition plot remains linear. However, these results alone are not sufficient to provide definite information regarding the preferential hydration-dehydration phenomenon in such systems.

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