Volumetric Properties of Hydrated Salts: Mixtures of the Hexahydrate of Nickel Nitrate with Cadmium Nitrate Tetrahydrate

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Densities of molten mixtures of $Cd(NO_3)_2 \cdot 4H_2O-Ni(NO_3)_2 \cdot 6H_2O$ were measured as a function of temperature and composition. The density and equivalent volumes varied linearly with temperature. Equivalent volume–composition plots are significant in view of the negative deviations from additive values and "breaks" around 30 and 80 mol % of nickel nitrate hexahydrate.

Growing interests in the use of molten hydrated salt systems, possessing supercooling and glass-forming tendencies, for certain specialized fields of research (*7*) and the observations that the volumes in such systems are nearly additive (*1, 3–5*) prompted this study regarding the measurement of densities of the mixed hydrated melts consisting of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$.

Experimental Section

The tetrahydrate of cadmium nitrate obtained from Reanal (Hungary) was of analaR grade. Hexahydrate of nickel nitrate was of LR (BDH, England) grade. An analytical cross check was made for water content of hydrate of cadmium nitrate by measuring the loss in the weight of a certain known weight of hydrate, on complete dehydration. Nickel content of $Ni(NO_3)_2 \cdot 6H_2O$ was determined by precipitating it as dimethylglyoxime. The analysis established the composition with maximum departure of ±0.01 for cadmium and ±0.02 for nickel salt. Mixtures of varying compositions were prepared separately by melting the requisite amounts of the components in Pyrex glass flasks with air-tight ground glass joints and digesting them at 60–70 °C for about 2–3 h.

The manometric densitometer originally designed by Husband (*2*) was modified so as to permit a direct measurement of the volume of a known amount of solution. The details regarding the densitometer, its calibration, and the measuring techniques, etc., were similar to those reported earlier (*3*). Temperatures were controlled and measured with a precision of ±0.1 °C.

Results and Discussion

The density and equivalent volume (V_e) data for all the mixtures studied are presented in Table I. The temperature dependence of density and equivalent volumes could be described by linear equations of the type

$$\rho(\mathrm{g\ cm^{-3}}) = \alpha - \beta t$$

$$V_e(\mathrm{cm^3\ equiv^{-1}}) = A + Bt$$

The constants α, β and A, B are the characteristic of the composition. These coefficients, recorded in Table II, were employed in computing the density/equivalent volume at certain temperatures of interest. The equivalent volume, of 69.45 $cm^3\ equiv^{-1}$, for molten $CD(NO_3)_2 \cdot 4H_2O$ at 75 °C obtained in this study is slightly higher than the value 68.22 $cm^3\ equiv^{-1}$ reported earlier (*3*) and 68.51 $cm^3\ equiv^{-1}$ obtained by Moynihan et al. (*6*). This

Table I. Density and Equivalent Volume Data for $Cd(NO_3)_2 \cdot 4H_2O-Ni(NO_3)_2 \cdot 6H_2O$ Mixtures

Mol/equiv % $Ni(NO_3)_2 \cdot 6H_2O$	Temp, °C	Density, g cm^{-3}	Equiv vol, cm^3 $equiv^{-1}$
0.0	41.4	2.2579	68.29
	45.5	2.2546	68.39
	50.0	2.2493	68.55
	55.0	2.2433	68.74
	60.0	2.2380	68.90
	65.0	2.2314	69.10
	70.0	2.2255	69.29
	76.3	2.2184	69.51
	80.7	2.2132	69.67
9.8	45.5	2.2380	68.52
	50.0	2.2313	68.73
	55.0	2.2247	68.93
	60.0	2.2187	69.12
	65.0	2.2127	69.31
	70.0	2.2062	69.51
	76.3	2.1991	69.74
	80.7	2.1938	69.91
19.4	28.0	2.2162	68.81
	30.5	2.2136	68.89
	33.8	2.2096	69.02
	38.7	2.2037	69.20
	43.5	2.1985	69.36
	49.0	2.1926	69.55
	53.1	2.1874	69.72
	58.5	2.1816	69.90
	64.3	2.1752	70.11
	70.0	2.1688	70.31
	76.0	2.1625	70.52
29.1	38.0	2.1420	70.77
	44.0	2.1356	70.99
	50.0	2.1293	71.20
	56.0	2.1237	71.38
	62.0	2.1165	71.63
	67.0	2.1115	71.80
	73.0	2.1053	72.01
	81.0	2.0958	72.33
40.0	30.0	2.0943	71.96
	31.0	2.0926	72.01
	36.0	2.0874	72.19
	41.0	2.0818	72.39
	46.0	2.0768	72.56
	51.0	2.0719	72.73
	56.0	2.0670	72.91
	61.0	2.0616	73.10
	66.0	2.0561	73.29
	76.0	2.0459	73.66
	81.0	2.0399	73.88

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Table I (continued)

Mol/equiv % $Ni(NO_3)_2{\cdot}6H_2O$	Temp, °C	Density, g cm^{-3}	Equiv vol, cm^3 $equiv^{-1}$
58.8	35.5	2.0265	73.52
	40.0	2.0215	73.71
	45.0	2.0160	73.91
	50.0	2.0105	74.11
	55.0	2.0050	74.31
	61.0	1.9984	74.56
	67.0	1.9919	74.80
	73.9	1.9844	75.08
	78.8	1.9791	75.29
	84.7	1.9727	75.53
69.5	33.5	1.9892	74.45
	37.5	1.9859	74.57
	41.6	1.9816	74.74
	46.5	1.9762	74.94
	51.2	1.9708	75.15
	54.7	1.9670	75.29
	59.5	1.9628	75.45
	67.0	1.9549	75.76
	75.5	1.9454	76.13
	81.5	1.9392	76.37
77.2	44.0	1.9353	76.16
	50.0	1.9290	76.41
	56.0	1.9227	76.66
	62.0	1.9164	76.91
	67.0	1.9112	77.12
	73.0	1.9053	77.36
	81.0	1.8969	77.70
79.5	33.5	1.9103	77.05
	37.5	1.9063	77.22
	41.6	1.9023	77.38
	46.5	1.8978	77.56
	51.2	1.8933	77.75
	54.7	1.8905	77.86
	59.5	1.8860	78.05
	67.0	1.8794	78.32
	75.5	1.8701	78.71
	81.5	1.8635	78.99

Table II. Density-Temperature and Equivalent Volume-Temperature Equations for $Cd(NO_3)_2{\cdot}4H_2O$-$Ni(NO_3)_2{\cdot}6H_2O$ Mixtures

Equiv % $Ni(NO_3)_2{\cdot}6H_2O$	Temp range, °C	Data points	ρ(g cm^{-3}) = $\alpha - \beta t$ α	$10^3\beta$	SE.	V_e(cm^3 $equiv^{-1}$) = $A + Bt$ A	$10^2 B$	SE.	V_e(75 °C), cm^3 $equiv^{-1}$
0.00	41-80	9	2.3068	1.159	0.0005	66.77	3.58	0.02	69.45
9.8	45-80	8	2.2936	1.242	0.0005	66.77	3.90	0.01	69.69
19.4	28-76	11	2.2475	1.123	0.0003	67.81	3.58	0.01	70.50
29.1	38-81	8	2.1827	1.065	0.0004	69.40	3.59	0.02	72.83
40.0	30-81	11	2.1252	1.048	0.0003	70.85	3.70	0.01	73.62
58.8	35-85	10	2.0652	1.093	0.0001	72.07	4.08	0.004	75.13
69.5	33-81	10	2.0249	1.051	0.0004	73.07	4.04	0.02	76.10
77.2	44-81	7	1.9808	1.037	0.0001	74.33	4.15	0.003	77.45
79.5	33-81	10	1.9424	0.957	0.0006	75.72	3.96	0.03	78.69
100.0	—	—	—	—	—	—	—	—	82.79[a]

[a] Reference 4.

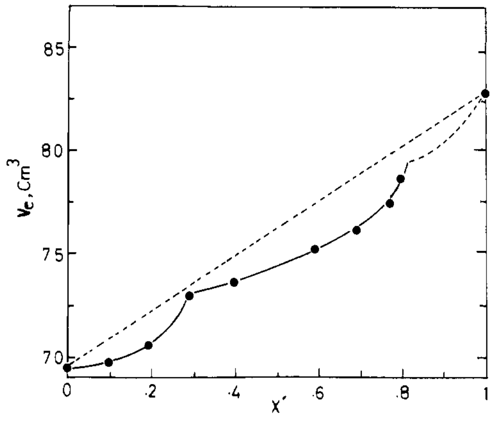

Figure 1. Variation of equivalent volume (75 °C) with mole fraction of $Ni(NO_3)_2{\cdot}6H_2O$ for the $Cd(NO_3)_2{\cdot}4H_2O$-$Ni(NO_3)_2{\cdot}6H_2O$ system.

could have resulted from small differences in the water content of the salts used.

The equivalent volume-equivalent fraction plots were drawn with the aid of previously reported (*4*) values for the equivalent volumes of $Ni(NO_3)_2{\cdot}6H_2O$. These appear to be significant in view of the observed negative deviations from the additive values. Small negative deviations (0.2-0.3% at $x'_{Cd^{2+}} = 0.5$) in the equivalent volumes of $Ca(NO_3)_2{\cdot}4.09H_2O + Cd(NO_3)_2{\cdot}4.07H_2O$ mixtures have also been reported by Moynihan et al. (*6*). It is of interest that the V_e-composition (mole fraction $Ni(NO_3)_2{\cdot}6H_2O$) plot (shown for 75 °C in Figure 1) shows "breaks" around 30 and 80 mol % of nickel nitrate hexahydrate. Near additive values at 30 and 80 mol % might be a reflection of the changes in the geometrical arrangement (tetrahedral $\rightleftharpoons$ octahedral) of the water molecules present in the first coordination of the two cations. However, further investigation of these systems is needed to obtain additional, direct evidences, for describing these peculiarities in terms of structural transformations or hydration/dehydration equilbria existing in such mixed hydrated melts.

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