

representing the root-mean-square deviation of the present data which are plotted in both figures. The data of Koenig (11) show the greatest deviations from the present work, especially at lower temperatures where his values are as much as 14% below ours. The Morrison and Johnstone data (12) also lie below our values, by up to 8% at the lower temperatures. The data of Wood and Caputi (19) are in better agreement: their two distilled water points which lie within our temperature range average 2.9% above our values, and their two seawater points within our temperature range average 1.9% below our values. However, the comparison of our data with those of Benson and Krause (1) is especially striking. Their seven distilled water measurements within our temperature range average just 0.24% above our values, with a maximum difference of 0.6%. Thus, although our methods give slightly different values for He and Ne solubilities (1), the two independent techniques show remarkably similar results for the solubility of krypton in distilled water.

Conclusions

The data reported here greatly improve our knowledge of the solubility of krypton, especially in seawater. The fitted values have an estimated accuracy of $\pm 0.4\%$ and a relative precision (\pm one standard deviation) of about 0.2%. The reliability of these results is strengthened by the accuracy of the solubilities of other gases measured by the same technique and by the close agreement with the recent data of Benson and Krause for the solubility of krypton in distilled water.

We have made a preliminary investigation of saturation anomalies shown by various measurements of krypton dissolved in the sea (2, 3, 10). Following the approach used earlier to study the relative enrichments of He, Ne, and Ar (4), an analysis of Ne, Ar, and Kr saturation anomalies shows that Kr fits a consistent

pattern of decreasing enrichment with increasing β , which may be explained by the injection of ~ 1 mL of air/kg of seawater in excess of equilibrium solubility. A detailed evaluation of these effects is reserved for later discussion.

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Additivity of Volumes in Hydrated Melts: Mixtures of Calcium and Cadmium Nitrate Tetrahydrates with Ammonium Nitrate

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Densities of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ systems have been measured at temperatures between 285 and 365 K and up to 60 equiv % of NH_4NO_3 . The systems obey the principle of additivity of volumes. Densities and equivalent volumes vary linearly with temperature.

It has been realized (1-4, 7, 9-17) that the studies of highly concentrated aqueous electrolyte solutions and hydrated melts are of importance in correlating the behavior of anhydrous molten salts and dilute aqueous electrolyte solutions. Recently, there has been special interest in the use of hydrated melts and highly concentrated aqueous electrolyte solutions, with super-cooling and glass-forming tendencies, in certain specialized fields of research. The principle of additivity of volumes has been found to be a useful approximation (2, 10) in evaluating the volumes at any desired composition from the limited data. The present investigation was aimed at exploring the validity of this approximation for $(\text{Ca}, \text{Cd})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ mixtures.

Experimental Section

Hydrated calcium and cadmium nitrates were AnalaR (BDH) grade. Water content of the salts, determined by volumetric titration with EDTA, was found to be 4 ± 0.01 mol/mol of cation. Ammonium nitrate, also AnalaR (BDH), was vacuum desiccated for 2-3 days and stored over anhydrous magnesium perchlorate until used. Mixtures of varying composition were prepared individually by fusing the calculated amounts of the components in a stoppered glass vessel and aging at 50-60 °C for about 4 h before use.

The manometric densitometer (β) was modified (10, 16) to allow direct measurement of the volume of a known amount of the melt with a precision of ± 0.005 cm³. Details regarding calibration of densitometer, dilation correction, thermostat bath, and temperature control unit have been described earlier (16). Data were taken both in heating and cooling cycles, and temperature was maintained with a precision of ± 0.05 °C.

Results and Discussion

The density and equivalent volume data for the different compositions of $(\text{Ca}, \text{Cd})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ mixtures con-

Table I. Least-Squares Equations of Density and Equivalent Volume Data for the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ System

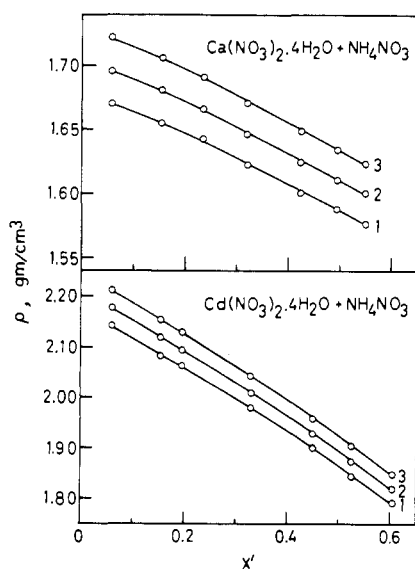
x'	Temp range (T, K)	Data points	$\rho = A - B(T - 300), \text{g cm}^{-3}$			$V = A' + B'(T - 300), \text{cm}^3 \text{equiv}^{-1}$			$10^4 \alpha,$ deg^{-1}
			A	$10^3 B$	10^3SE	A'	$10^2 B'$	SE	
0.058	290-365	15	1.725 20	0.884 08	0.16	67.159 15	3.541 67	0.006	5.20
0.109	290-365	15	1.717 59	0.846 91	0.13	66.321 70	3.312 39	0.005	5.00
0.156	290-365	15	1.707 20	0.822 05	0.28	65.688 58	3.242 34	0.011	4.89
0.197	290-365	15	1.700 99	0.807 85	0.04	64.997 53	3.176 14	0.008	4.81
0.235	290-365	15	1.693 48	0.811 96	0.26	64.442 00	3.141 85	0.010	4.86
0.269	290-365	15	1.690 76	0.834 79	0.06	63.775 12	3.201 02	0.002	5.01
0.330	290-365	15	1.673 10	0.807 70	0.05	63.072 51	3.132 39	0.002	4.90
0.381	290-365	15	1.662 31	0.790 11	0.03	62.314 01	3.041 73	0.002	4.82
0.424	290-365	15	1.650 38	0.799 37	0.06	61.758 70	3.048 81	0.002	4.91
0.463	290-365	15	1.647 98	0.792 19	0.04	60.972 24	2.996 20	0.005	4.88
0.496	295-365	14	1.636 94	0.782 53	0.03	60.602 74	2.987 61	0.002	4.85
0.525	295-365	14	1.630 60	0.781 55	0.04	60.151 84	2.969 55	0.002	4.87
0.551	300-365	13	1.625 29	0.774 85	0.03	59.734 24	2.938 94	0.002	4.80

Table II. Least-Squares Equations for Density and Equivalent Volume Data of the $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ System

x'	Temp range (T, K)	Data points	$\rho = A - B(T - 300), \text{g cm}^{-3}$			$V = A' + B'(T - 300), \text{cm}^3 \text{equiv}^{-1}$			$10^4 \alpha,$ deg^{-1}
			A	$10^3 B$	10^3SE	A'	$10^2 B'$	SE	
0.060	285-365	16	2.215 78	1.161 92	0.07	67.569 82	3.646 05	0.009	5.32
0.156	285-365	16	2.156 11	1.114 69	0.34	66.153 52	3.489 60	0.014	5.25
0.197	285-365	16	2.132 57	1.101 29	0.40	65.450 88	3.448 37	0.014	5.24
0.330	285-365	16	2.045 57	1.048 56	0.31	63.407 70	3.315 75	0.012	5.18
0.363	285-365	16	2.021 71	1.043 28	0.13	62.957 93	3.338 68	0.003	5.23
0.437	285-365	16	1.970 73	1.011 48	0.20	61.804 55	3.239 05	0.010	5.18
0.451	285-365	16	1.962 66	1.003 81	0.40	61.539 43	3.211 76	0.016	5.20
0.525	285-365	16	1.908 78	0.996 44	0.11	60.367 42	3.238 16	0.004	5.31
0.509	285-365	16	1.919 23	0.987 01	0.17	60.655 62	3.183 16	0.007	5.22
0.604	295-365	14	1.850 96	0.944 52	0.16	59.106 14	3.088 98	0.007	5.19

Table III. Density-Equivalent Fraction Equations for $(\text{Ca}, \text{Cd})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ Mixtures

T, K	$\rho = a + bx' + (x'^2 + dx'^3), \text{g cm}^{-3}$				SE
	a	b	c	d	
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$					
303.2	1.7303	-0.1226	-0.2263	0.1719	0.0019
333.2	1.7014	-0.0829	-0.3384	0.2802	0.0020
363.2	1.6762	-0.0814	-0.3282	0.2675	0.0018
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$					
303.2	2.2472	-0.5737	-0.1532	0.0134	0.0009
333.2	2.2108	-0.5490	-0.2001	0.0602	0.0010
363.2	2.1755	-0.5456	-0.1605	0.0171	0.0017

Figure 1. Density vs. equivalent fraction isotherm for $(\text{Ca}, \text{Cd})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ systems: 1, 303.2 K; 2, 333.2 K; 3, 363.2 K.

taining up to 60 equiv % of NH_4NO_3 were obtained at temperatures ranging between 288.2 and 363.2 K. Equivalent volumes were calculated using the mass of the mixture containing 1 mol of NO_3^- ion; the implication being that the number of these ions, the main space-filling species, would then be independent of the composition for the "per equivalent" unit and thus the changes in the volumes with composition will reflect directly the changes in the packing density (cf. 5, 15).

Temperature Dependence. Variation of density and equivalent volumes with temperature was linear and obeyed the equation of the type

$$\rho = A - B(T - 300)$$

$$V = A' + B'(T - 300) \quad (1)$$

Values of coefficients A , B and A' , B' at different compositions, evaluated by the least-squares fitting of the data using the IBM 360/44 data processing system, and the standard deviations are listed in Tables I and II. The coefficient B of the ρ - T equation is related to the expansion coefficient (α) of the mixture by the relation

$$\alpha = B/\rho \quad (2)$$

Mean values of α for the mixtures, over the temperature range of study, are also included in Tables I and II. These are seen to be of the same order; the values for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ being $(4.91 \pm_{-0.11}^{+0.29}) \times 10^{-4}$ and $(5.23 \pm_{-0.05}^{+0.09}) \times 10^{-4} \text{ deg}^{-1}$, respectively.

Coefficient B' for the V - T equation, the "mean equivalent expansivity", decreases with the increase in NH_4NO_3 content in the mixture. A smooth change over a sixfold change in concentration indicates the absence of any significant structural changes on the addition of NH_4NO_3 .

Using the free volume concept (δ), the equivalent volume may be expressed in terms of the van der Waals volume (V_0) and the free volume (V_f)

$$V = V_0 + V_f \quad (3)$$

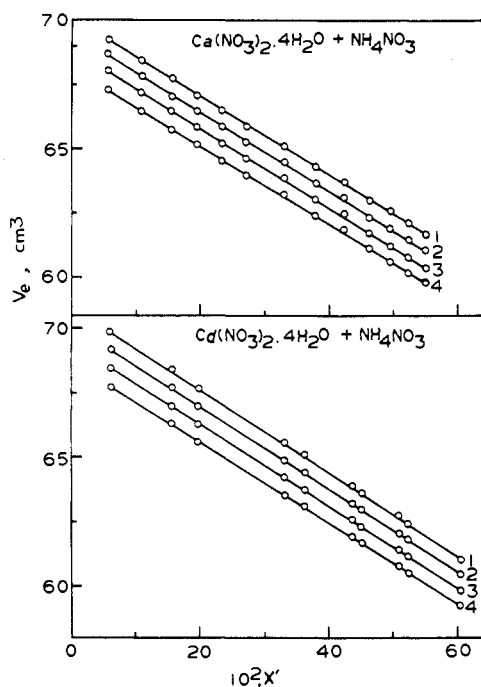


Figure 2. Equivalent volumes vs. equivalent fraction isotherms for $(\text{Ca,Cd})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ systems: 1, 303.2 K; 2, 323.2 K; 3, 333.2 K; 4, 363.2 K.

Table IV. Partial Equivalent Volume-Temperature Equations for $\text{M}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ Systems

System	$\bar{V}_{\text{M}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}}$	$\bar{V}_{\text{NH}_4\text{NO}_3}$
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$	$67.96 + (3.45 \times 10^{-2})(T - 300)$	$53.07 + (2.5 \times 10^{-2})(T - 300)$
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$	$68.55 + (3.65 \times 10^{-2})(T - 300)$	$53.03 + (2.65 \times 10^{-2})(T - 300)$

Table V. Comparison of Computed Equivalent Volumes (323.2 K) with Literature Data

$\bar{V}_{\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}}$ $\text{cm}^3 \text{equiv}^{-1}$	$\bar{V}_{\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}}$ $\text{cm}^3 \text{equiv}^{-1}$	$\bar{V}_{\text{NH}_4\text{NO}_3}$ $\text{cm}^3 \text{equiv}^{-1}$	Ref
68.76	69.40	53.64	Present study
68.37	67.40		Jain (10)
68.09			Angell (7)
68.37			Moynihan (11)
68.50	68.08		Moynihan et al. (12)
		52.30	Sharma and Gaur (16)

since V_0 would be constant for a given composition, the temperature dependence of V is given by

$$dV/dT = dV_f/dT \quad (4)$$

If α is the expansion coefficient, V_f is given by

$$V_f = V_0 \left[\exp \int_{T_0}^T \alpha dT - 1 \right] \quad (5)$$

or

$$V_f = V_0 [\exp(\alpha \Delta T) - 1] \quad (6)$$

where ΔT is the difference in temperature between the temperature of study (T) and the temperature at which free volume begins to appear (T_0). Expanding the exponential and neglecting higher powers

$$V_f = V_0 \alpha \Delta T \quad (7)$$

$$dV_f/dT = V_0 \alpha \quad (8)$$

Thus, the temperature dependence of equivalent volume would be proportional to the van der Waals volume of the system, which decreases with the increase in NH_4NO_3 content of the system. This appears logical as the larger hydrated cations $\text{Ca}(\text{H}_2\text{O})_4^{2+}$ and $\text{Cd}(\text{H}_2\text{O})_4^{2+}$ are replaced by the relatively much smaller cation (NH_4^+). This fact is supported by the values of the parameter B' , which represents the derivative dV/dT .

Composition Dependence. Typical variation of density (ρ) with an equivalent fraction of NH_4NO_3 (x') at 303.2, 333.2, and 363.2 K is shown in Figure 1. The plots are nonlinear; convexity toward the composition axis may be a reflection of increased packing density of the system. Variation of density with composition could be expressed by a polynomial equation of the type

$$\rho = a + bx' + cx'^2 + dx'^3 \quad (9)$$

values of coefficients a , b , c , and d are included in Table III.

Plots of equivalent volumes vs. equivalent fraction are linear (Figure 2), providing support to the law of additivity of volumes. Since the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ systems are volumetrically ideal, the partial equivalent volumes of the components will be constant over the entire range of concentration and these should be equal to the equivalent volumes of pure components. Partial equivalent volumes were evaluated from equivalent volume-composition isotherms (Figure 2) by the graphical extrapolation method and also by least-squares fitting of $V-x'$ data into the equation

$$V = P + Qx' \quad (10)$$

The parameter P will then give the partial equivalent volume of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(P + Q)$ the partial equivalent volume of NH_4NO_3 . Equations representing the temperature dependence of the computed partial equivalent volumes are presented in Table IV. The slightly higher value of the equivalent volume of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ may be due to the small difference in the size of hydrated Ca^{2+} (3.75 Å) and Cd^{2+} (3.77 Å) ions. The partial equivalent volumes computed in this study are compared (Table V) with the results reported earlier (2, 10, 12, 16). The agreement between the extrapolated and the directly measured volumes appears to be reasonable.

The additivity of volumes in the systems $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and the fact that computed equivalent volumes are in good agreement with those of pure components suggest that the NH_4^+ ion does not compete for water of hydration originally present in the coordination of divalent cations (1, 2).

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