CONDUCTIVITY, DENSITY AND VISCOSITY OF MOLTEN HYDRATED SALT SYSTEMS: MIXTURES OF HYDRATED NITRATES OF THE ALUMINUM AND IRON, WITH CALCIUM, CADMIUM, MAGNESIUM, AND ZINC NITRATE HYDRATES

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ABSTRACT

Conductivity, density and viscosity of title systems were studied at temperatures in the range 270 to 365 K over a wide range of composition. Volumes of cerium-containing mixtures exhibited large negative deviation from additivity while those of iron- and aluminum-containing systems were nearly additive. Temperature-dependence of conductivity and viscosity was consistent with VTF equation. The results have been interpreted considering preferential hydration of trivalent cations and presence of co-ordinated and lattice water.

INTRODUCTION

The behaviour of molten hydrated salts of divalent cations have been explained considering the existence of weak field cations of the type M(H$_2$O)$_m^{2+}$ and anions. These solutions have been considered as hydrous melts since molten salt models have frequently been used to interpret the thermodynamic, transport and spectral behaviour. Several hydrated salts and mixtures show strong supercooling and glass-forming tendencies, enabling measurements well below the freezing point and thus over a wide range of temperature. The principle of additivity of volumes has generally been found to be applicable, at least to a first approximation. Conductivity and viscosity of the mixtures have been found to be dependent on the composition because of the difference in ion-ion and ion-water interactions.

In continuation of our studies in several hydrous melts and highly concentrated electrolyte solutions, results of density, conductivity, and viscosity of hydrated molten nitrates of aluminum and iron with calcium, cadmium, zinc, and magnesium nitrate hydrates are presented in this paper.

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EXPERIMENTAL

All salts were of AnalaR (BDH) grade purity; water content of the salts, determined by volumetric titration with EDTA, were within ±0.01 of the stoichiometric value. Mixtures of varying composition were prepared individually by mixing calculated amounts of components, fusing in a stoppered glass vessel, filtering and maturing at 5-10° above the melting point for 3 hrs.

The densimeter was essentially of the type used by Husband & McAuley (1,2), modified (3) to accommodate a wider range of temperatures. A Beckman conductivity bridge (Model RC-18A) based on Wien's bridge principle, provided with a CRT null detector and Wagner ground, operated at an a.c. frequency of 1 KHz, was used to measure the solution resistance. A decade capacitance (Cp) box was connected in parallel with a resistance (Rp) box in the measuring arm of the bridge, and the resistance in the ratio arms were matched. Considering the cell as a series combination of a resistance (Rs) and a capacitance (Cs), at the balance point one has:

\[ R_s = \frac{R_p}{1 + (R_p C_p 2\pi f)^2} \]

where f is the frequency of the a.c. signal in Hz. A dip-capillary type conductivity cell was used. A three-limb Cannon-Ubbelhode-Flenske type viscometer used to measure viscosity was calibrated with triple distilled water, 20% and 40% sucrose and 98% glycerol solutions.

DISCUSSION

In these systems, the size of the common anion is large relative to other ions in the system; thus the common anion may be considered as the main space-filling species. Also, water of hydration is associated, almost fully, with the cation (4). Taking the analogy from concentrated aqueous electrolyte solutions, water may be differentiated as co-ordinated water forming the first hydration shell around the cation and the lattice water constituting the second, third, etc shells, possibly the formation of H-bonded dimers, trimers or polymers (clusters) of water molecules. The complexing nature of cations, and/or ion-ion interactions may lead to the formation of contact-ion-pairs (CIP) or solvent-separated ion-pairs (SSIP) in solution. Also, differences in cationic potentials may lead to hydration-dehydration equilibria of the type (5)

\[ M_2(\text{H}_2\text{O})_{m}^{2+} + M_1(\text{H}_2\text{O})_{n}^{2+} \rightleftharpoons M_2(\text{H}_2\text{O})_{m-x}^{2+} + M_1(\text{H}_2\text{O})_{n+x}^{2+} \]

on addition of divalent nitrate hydrate* to the trivalent nitrate hydrate. In this lattice, water from the hydration sphere of the trivalent cation is accommodated as

*Subscripts 1 and 2 refer to divalent and trivalent cations respectively.
coordinated water if the available water of hydration of the latter is insufficient to complete the primary hydration shell or is taken up as lattice water of the latter. The various interactions affect the packing density and the transport behaviour of species in solution.

Volumetric behaviour of hydrated molten salts and mixtures may be discussed in terms of a reference state e.g., molten aluminum or iron(III) nitrate hydrate the implication being that at temperatures 5-50° away from the melting point and within the composition range, as used, the basic microscopic lattice structure of this component can still be considered to be predominant. The addition of the divalent metal nitrate hydrate perturbs or modifies the structure according to different interactions.

1. \((V - X_1)\) isotherms

Typical results of the variations of molar volume \((V)\) at 313.2, 333.2 and 353.2 K for \(\text{Al(NO}_3\text{)}_2 \cdot 10\text{H}_2\text{O} - \text{(Ca, Cd, Zn, Mg) (NO}_3\text{)}_2 \cdot 4,6 \text{H}_2\text{O}\) (Fig. 1) show a nearly-linear decrease with increase in \(X\). Strong polarization of \text{NO}_3^- ion towards hydrated \(\text{Al}^{3+}\) would lead to \(\text{Al}^{3+} - (\text{H}_2\text{O})_{n-x} - \text{NO}_3^-\) interaction forming SSIP and consequent displacement of some lattice water from the hydration sphere of \(\text{Al}^{3+}\). The water thus released would be accommodated in the (primary) hydration sphere of \(\text{Ca}^{2+}\); also, \text{NO}_3^- would be attracted toward the positive part of dimeric water \((\text{OH}^- - \text{H}_3\text{O}^+)\). Consequently, the packing density would increase and \(V\) would decrease with increasing \(X\) as was observed.

For nearly-ideal systems, partial molar volumes \(V_1\) and \(V_2\) could be evaluated by graphical extrapolation. Alternatively, \(V\) could be expressed as a linear function of the mole fraction of one of the components, (say 1) by

\[
V = E + FX_1
\]

from which, one has
\[
E = \overline{V}_2 \quad \text{and} \quad F = \overline{V}_1 - \overline{V}_2
\]

Iron being a d-block element would, relative to Al, show stronger tendency to form SSIP and also have stronger coordination bonds with water molecules. The difference in behaviour, not obvious in \(V\)-X plots, shows up in the partial volume parameters (Tables 1 and 2). Except for \(\text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) -containing mixtures (vide infra), \(V_1\) for other divalent metal nitrate hydrates in \(\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) -mixtures is 2-5% more than in \(\text{Al(NO}_3\text{)}_3 \cdot 10\text{H}_2\text{O}\) mixtures.
2. \((p, V) - T\)

At a given composition, both \(p\) and \(V\) varied linearly with \(T\) and could be least-square-fitted with an equation of the type

\[
p(V) = A(A') + B(B') (T - 300)
\]

where the parameters \(A, A', B, B'\) are constants, characteristic of the system and its composition. The fits enabled evaluation of expansion coefficient, \(\alpha = (-1/p \, (d\rho/dT))\) which equals \(B\), and molar thermal expansibility, \(V_E (= (dV/dT)_X)\) which equals the parameter \(B'\).

\(V_E\) and \(\alpha\) are useful in interpreting structural changes with changes in composition and temperature. The molar volume of the mixture can be expressed as a sum of a van der Waals \((V_0)\) volume and a free \((V_f)\) volume due to an increase in temperature from a specified value:

\[
V = V_0 + V_f
\]

For a given composition, variation of the volume with temperature is identical to that of the free volume, since \(V_0\) is not a function of temperature:

\[
\frac{dV}{dT} = \frac{dV_f}{dT} = B'
\]

\(V_f\) can also be expressed as:

\[
V_f = V_0(\exp \int_T^{T_0} \alpha dT - 1)
\]

where \(T_0\) is the temperature above which free volume is formed. If \(\Delta T\) is the difference between temperature of study and \(T_0\), one has:

\[
V_f = V_0 \exp[\alpha \Delta T] - 1) \approx \alpha V_0 \Delta T
\]

and

\[
\frac{dV_f}{dT} = V_E = V_0 \alpha
\]

Typical data of mixtures of \(\text{Al(NO}_3)_3 \cdot 10\text{H}_2\text{O}\) with divalent metal nitrate hydrates (Fig. 2) show a decrease in \(V_E\) with \(X\). Changes in \(\alpha\) are relatively small; a decrease in \(V_E\) could be considered to arise largely due to a decrease in

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The latter results from a decrease in the number of NO$_3^-$ ions, the main space-filling species and also the number of water molecules per mole of the mixture. A slightly different trend for Zn-system (also Fig. 2) may be explained due to complexing nature of Zn$^{2+}$ and the reported CIP Zn$^{2+}$ – NO$_3^-$ formation, in concentrated zinc nitrate solutions. This would result in increase in $V_0$ and hence a smaller decreasing trend in $V_F$.

According to the Born model of ion-solvent interaction, $\alpha$ has contributions both from configurational and vibrational factors. Molten hydrated salts in which the water of hydration is almost wholly associated with the cations, have low expansion coefficients. Addition of divalent cation to Al$^{3+}$-containing systems would decrease the electrostricting affect. This would increase free existence of dimers, trimers, etc of water increasing the configurational contribution to $\alpha$, as observed.

A slightly higher slope for Zn-containing systems is consistent with the formation of CIP Zn$^{2+}$ – NO$_3^-$ and consequent displacement of some of the coordinated water molecules of Zn$^{2+}$ at lattice water. Increase in $\alpha$ with temperature in all cases results from a larger vibrational contribution of water molecules to $\alpha$.

3. ($\kappa$, $\eta$) – X isotherms

Typical variations of $\kappa$ for Al(NO$_3$)$_3$·10H$_2$O – Ca(NO$_3$)$_2$·4H$_2$O system at 313.2, 333.2 and 353.2 K showed an initial decrease in $\kappa$ up to $\omega = 80$ mole of Ca$^{2+}$; on further addition of Ca$^{2+}$, $\kappa$ is almost unaffected. This is consistent with strong Al$^{3+}$ (H$_2$O)$_{n-x}$NO$_3^-$ interaction forming SSIP and the displacement of some lattice water from hydration sphere of Al$^{3+}$ to new sites in the (primary) hydration sphere of Ca$^{2+}$ forming species of type Ca$^{2+}$ (OH$^-$–H$_3$O$^+$)NO$_3^-$. Both would result in a decrease in $\kappa$ and an increase in $\eta$ as observed. At higher concentration, a saturation in Ca$^{2+}$ (OH$^-$–H$_3$O$^+$)NO$_3^-$ interaction and also the reported formation of the CIP, Ca$^{2+}$·NO$_3^-$ – (H$_2$O), would result in a decrease in $\kappa$ and increase in $\eta$, as observed. It may be noted that formation of CIP does not contribute significantly to conductivity but affects the viscosity of the system much more.

In the Fe(NO$_3$)$_3$·6H$_2$O – Mg(NO$_3$)$_2$·6H$_2$O system, a small decrease in $\kappa$ and an increase in $\eta$ are observed. It has been shown that Mg$^{2+}$ does not form CIP to any significant extent but due to relatively higher cationic potential, would have strong tendency to form weak-field cation of the type Mg(H$_2$O)$_3$$^{2+}$. Addition of Mg$^{2+}$ would change the ion-water interactions which are of smaller magnitude and hence a smaller variation in $\kappa$ and $\eta$ is shown.
4. \((A, \phi) - T\) data

Temperature variation of \(A\) and \(\phi\) were non-Arrhenian, and could be satisfactorily expressed by the VTF equation (6-8)

\[
y(A, \phi) = A_y \exp \left( \frac{-B_y}{T - T_0, y} \right)
\]

where \(A_y\) and \(B_y\) are empirical parameters characteristic of the system purity and the transport property; and \(T_0\) is the temperature at which the transport property approaches a limiting value. Theoretical basis was provided by the free volume model (9) and the cooperative rearrangement (10) theory; \(T_0\) can be interpreted as the temperature above which free volume begins to form or at which the configurational entropy of the system is zero. Computer simulation of \(A, \phi - T\) data was done to evaluate the parameters, \(A_y, B_y\) and \(T_0\). Typical parameters for conductivity data for \(\text{Al(NO}_3\text{)}_3 \cdot 10\text{H}_2\text{O} - \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) and viscosity data for \(\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} - \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) were evaluated.

\(T_0\) has been considered as a useful parameter for the observed changes in the total interaction energy of the system. Ionic systems in which principal interactions are ion-ion type have maximum value of \(T_0\). On the other extreme are molecular liquids where principal interactions are of van der Waal type. Molten hydrated salts and highly concentrated aqueous electrolyte solutions have \(T_0\) in the intermediate range. In these, the interaction energy is determined by ion-ion, ion-water and water-water interactions. Since \(T_0\) depends on the total interaction energy, which is a function of \(X\), a study of the variation of \(T_0\) with \(X\) has been carried out.

In \(\text{Al(NO}_3\text{)}_3 \cdot 10\text{H}_2\text{O} - \text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) system, \(T_0\) increases with \(X\). It has been proposed earlier that addition of calcium nitrate results in increased interactions between \(\text{Al}^{3+}\) and \(\text{NO}_3^-\) decreasing \(\text{Al}^{3+} - \text{H}_2\text{O}\) interactions. Also \(\text{Ca}^{2+} - \text{H}_2\text{O}\) interaction decreases due to formation of dimeric water. The observed trend of increasing \(T_0\) with \(X\) is consistent with the predominance of ion-ion interactions. In the \(\text{Al(NO}_3\text{)}_3 \cdot 10\text{H}_2\text{O} - \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) system, an almost constant \(T_0\) means that the change in magnitude of interactions is small since the predominant interactions are ion-water type. This is also supported by conductance-composition isotherms.

Hydrated ferric nitrate-containing systems do not show significant changes in \(T_0\) with \(X\) since, due to complexing nature of \(\text{Fe}^{3+}\), change in magnitude of ion-ion interactions is small. It may be recalled that in discussing conductivity - composition isotherms, the main interactions considered were ion-water and water-water type, which do not influence the value of \(T_0\) significantly.
Volume dependence of the transport properties has also been fitted into Doolittle equation (11) which is similar to VTF equation

\[ M = A_M' \exp \left( \frac{-B'}{V - V_o,M} \right) \]

where \( M \) is either \( A \) or \( \phi \) and \( V_0 \) is the intrinsic volume, which by analogy to VTF eqn is the molar volumes at \( T_0 \). Evaluated values of \( V_0 \) are nearly the same from both conductivity and fluidity data.

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Table I. Partial Molar Volumes of Components of
Al(NO₃)₃.10 H₂O + M(NO₃)₂.R H₂O Systems

| M(NO₃)₂.RH₂O | Temp (K) | V₁ cm⁻³ mol⁻¹ | V₂ cm⁻³ mol⁻¹ |
|--------------|----------|---------------|---------------|
| Ca(NO₃)₂.4H₂O |          |               |               |
| 313.2        | 252.53   | 134.59        |
| 333.2        | 254.47   | 135.80        |
| 353.2        | 256.79   | 136.90        |
| 313.2        | 251.61   | 136.16        |
| 333.2        | 253.72   | 137.50        |
| 353.2        | 255.73   | 138.79        |
| Cd(NO₃)₂.4H₂O |          |               |               |
| 313.2        | 251.61   | 136.16        |
| 333.2        | 253.72   | 137.50        |
| 353.2        | 255.73   | 138.79        |
| 313.2        | 253.44   | 157.33        |
| 333.2        | 255.12   | 159.23        |
| 353.2        | 257.78   | 161.07        |
| Zn(NO₃)₂.6H₂O |          |               |               |
| 333.2        | 252.64   | 167.06        |
| 353.2        | 255.57   | 168.91        |
| Mg(NO₃)₂.6H₂O |          |               |               |
| 333.2        | 252.64   |               |
| 353.2        | 255.57   |               |

a) Sharma, Jain, Gaur *J. Chem. Eng. Data*, 23 (1978) 2
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Table II. Partial Molar Volumes of Components for Fe(NO₃)₂·9H₂O + M(NO₃)₂·RH₂O System

| M(NO₃)₂·RH₂O   | Temp (K) | V₁  cm³ mol⁻¹ | V₂  cm³ mol⁻¹ |
|---------------|---------|--------------|--------------|
| Ca(NO₃)₂·4H₂O | 313.2   | 241.37d      | 137.59       | (135.80)a |
|               | 333.2   | 244.50       | 138.84       |            |
|               | 353.2   | 247.80       | 140.04       |            |
| Cd(NO₃)₂·4H₂O | 313.2   | 240.82       | 137.10       | (136.71)a |
|               | 333.2   | 243.97       | 138.39       |            |
|               | 353.2   | 247.24       | 139.68       |            |
| Zn(NO₃)₂·6H₂O | 313.2   | 239.70       | 165.10       | (161.37)b |
|               | 333.2   | 242.82       | 167.05       |            |
|               | 353.2   | 246.06       | 168.98       |            |
| Mg(NO₃)₂·6H₂O | 313.2   | 241.82       | 152.56       | (166.88)c |
|               | 333.2   | 244.42       | 160.43       |            |
|               | 353.2   | 247.69       | 161.91       |            |

a) Sharma, Jain, Gaur J. Chem. Eng. Data, 23 (1978) 72  
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**Fig. 1.** Isotherms of molar volume \((V)\) vs. mole fraction of divalent cation \((X)\) for \(\text{Al(NO}_3\text{)}_3\cdot 10\text{H}_2\text{O} + \text{M(NO}_3\text{)}_2\cdot n\text{H}_2\text{O}\) systems: (I) \(313.2\) K; (II) \(333.2\) K; (III) \(353.2\) K. Mole fraction axis scale: (I) for Ca, (II) for Cd, (III) for Zn, (IV) for Mg containing mixtures.

**Fig. 2.** Composition variation of thermal expansion coefficient \((\alpha)\) and molar expansivity \((V_2)\) of \(\text{Al(NO}_3\text{)}_3\cdot 10\text{H}_2\text{O} + \text{M(NO}_3\text{)}_2\cdot n\text{H}_2\text{O}\) Systems at 300 K.