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MOLTEN SALT HYDRATES. I. AN APPROACH TO DETERMINING THE NATURE OF THE COORDINATION SPECIES PRESENT

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ABSTRACT

Recently published data on densities for twelve molten salt hydrates have been used in conjunction with estimated radii of metal ions and ligands to calculate masses of the coordination units in these systems. In almost all cases, the results are in accord with the experience of coordination chemistry and with expected coordination numbers. For some systems, the possible existence of certain species is postulated.

INTRODUCTION

Molten salt hydrates of the type $M(NO_3)_x \cdot yH_2O$ (M = Ca, Cr, Zn, Ni, etc.; x = 2 or 3; y = 4, 6, or 9) provide an interesting bridge between the behavior of concentrated salt solutions and molten salts. Theoretical studies have provided a transport model that considers properties where no bulk solvent is present (Angell and Bressel, 1972; Sare, Moynihan, Smalley, and Angell, 1973). Recently, physical properties have been reported for a number of molten salt hydrates (Jain, 1977, 1978). The data reported show non-Arrhenian behavior of fluidities and linear dependence of densities on the temperature.

In molten salt hydrates, the metal ion is present in a weak field environment as a large spherical cation (Angell, 1965; Moynihan, 1966). It is also considered that there is competition between water and anions for the coordination sites (Jain, 1978). In this paper, we present an elementary analysis of the nature of the coordination unit present in these systems.

METHODS

A coordination unit is assumed to exist which consists of the metal ion and the water molecules or anions of the primary coordination sphere. This unit may be a complex ion or a neutral species depending on the charge on the metal ion and the number of anions in the coordination sphere. For the calculations used here, it is assumed that the density of the coordination unit is the same as that of the bulk melt. This approximation, while seemingly severe is reasonable for some of the molten salt hydrates because all the water molecules and anions are coordinated to the metal. In other cases, it is likely that the density is little affected by free space or free solvent. This will be shown later by specific calculated results.

The volume of the spherical coordination unit is given by $V = 4\pi r^3/3$, and the mass of one spherical unit is $m = M/N_o$ where r is the radius, M is the molecular weight, and N_o is Avogadro's number. Thus, the density of the coordination unit is

$$\rho = \frac{3M}{4\pi r^3 N_o}$$

The molecular weight of the unit is given by

$$M = \frac{4\pi r^3 N_o \rho}{3}$$

Knowing the density of the sphere and its radius permits the calculation of the molecular weight of the coordination unit. The effective radii of the coordination spheres were estimated by means of the expression

$$r_{unit} = r_{metal\ ion} + 2\, r_{ligand}$$

with the metal ion and ligand radii taken from Huheey (1972) and Wells (1975). The densities at 60° were obtained from the density and temperature dependent parameters published by Jain (1977, 1978).

RESULTS AND DISCUSSION

In view of the severity of the assumptions made, it might be expected that the calculated mass of the cation unit present in a molten salt hydrate would bear little resemblance to that predicted on the basis of coordination chemistry. Consider, for example, the salts $FeCl_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 6H_2O$. On the basis of coordination chemistry, it would be expected

that even in the solid the coordination unit would be $[Fe(H_2O)_6]^{3+}$. Table 1 shows the experimental density data and estimated radii for these compounds as molten salt hydrates. Using those data, the calculated mass of the coordination unit is 169 amu while the actual value for $[Fe(H_2O)_6]^{3+}$ is 164 amu. Clearly, assuming a spherical coordination unit having the density of the melt results in a calculated unit mass approximating closely that expected on the basis of coordination chemistry.

In the case of $ZnCl_2 \cdot 4H_2O$, the calculated radius of the cation is 3.54 Å, assuming the radius to be made up of $(r_{Zn^{2+}} + 2\ r_{H_2O})$. The experimental density is 1.8090 g/cm³ so that a coordination unit mass of 202 amu is calculated. This calculated mass corresponds to that for the four molecules of water, the Zn^{2+} ion, and 1.8 chloride ions in the coordination sphere. For a coordination unit consisting of $[Zn(H_2O)_4Cl_2]$, the expected mass would be 207.4 amu. This discrepancy, while small, could be due to an equilibrium between tetrahedrally and octahedrally coordinated Zn^{2+} since the mass calculated from the density is slightly lower. The calculated mass of the coordination unit present in molten $Mn(NO_3)_2 \cdot 6H_2O$ is 210 amu. This corresponds almost exactly to $[Mn(NO_3)(H_2O)_5]^+$.

For $Cr(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and some of the other compounds, the data shown in Table 1 indicate that the calculated mass of the coordination unit agrees well with expectations based on coordination chemistry. In general, coordination numbers of six are indicated for most of the compounds.

For $Ni(NO_3)_2 \cdot 6H_2O$, the density and radius support a value of 192 amu while the unit $[Ni(H_2O)_6]^{2+}$ has a mass of 167 amu. A coordination unit of $[Ni(NO_3)(H_2O)_4]^+$ would have a mass of 193 amu. Whether this species is actually present or not is unknown. It is possible that the actual species present represent an equilibrium mixture of species including both four and six coordinated complexes. In the case of $Ca(NO_3)_2 \cdot 4H_2O$, the calculated mass of the coordination unit is 235 amu while the formula weight of the compound is 236 amu. It is apparent that this compound gives results that indicate that the melt contains $[Ca(H_2O)_4(NO_3)_2]$. A similar result is obtained for $Cd(NO_3)_2 \cdot 4H_2O$.

For most of the compounds considered, it is readily apparent that the coordination units estimated on the basis of their masses calculated using densities and radii are in accord with experience based on coordination chemistry. In the few cases where there is a discrepancy, other simple structures could account for the mass of the coordination unit. While these results do not prove the presence of any

Table 1. Radii, densities, unit masses, and proposed contents of the coordination units in several molten salt hydrates.

Compound	r_{metal}, Å	r_{unit}, Å	ρ, g/cm³ at 60°	M, g/mole	Proposed Coord. Unit* $H_2O(j)$	Proposed Coord. Unit* Anion(k)	Coord. No.
$Mn(NO_3)_2 \cdot 6H_2O$	0.80	3.60	1.7823	210	5.0	1.0	6
$Ca(NO_3)_2 \cdot 4H_2O$	0.99	3.79	1.7140	235	4.0	2.0	6
$ZnCl_2 \cdot 4H_2O$	0.74	3.54	1.8090	202	4.0	1.8	6
$Cd(NO_3)_2 \cdot 4H_2O$	0.97	3.77	2.2536	305	4.0	1.9	6
$Ni(NO_3)_2 \cdot 6H_2O$	0.70	3.50	1.7709	192	4.0	1.0	5
$Co(NO_3)_2 \cdot 6H_2O$	0.72	3.52	1.7743	195	6.0	0.5	6
$Zn(NO_3)_2 \cdot 6H_2O$	0.74	3.54	1.8006	201	4.1	1.0	5
$Mg(NO_3)_2 \cdot 6H_2O$	0.65	3.45	1.5659	162	4.0	1.1	5
$Cr(NO_3)_3 \cdot 9H_2O$	0.64	3.44	1.6735	172	6.0	0.2	6
$Fe(NO_3)_3 \cdot 6H_2O$	0.67	3.47	1.5995	169	6.0	0.1	6
$FeCl_3 \cdot 6H_2O$	0.67	3.47	1.5965	169	6.0	0.1	6
$Al(NO_3)_3 \cdot 9H_2O$	0.50	3.30	1.5432	140	6.0	0.1	6

*The general formula is $M(H_2O)_j(Anion)_k$

species, it is unlikely that the agreement between mass calculated and the mass of known structures is entirely fortuitous. Clearly, a great deal more study will be necessary to confirm the structure of the coordination unit present and some units may even be transitory in nature. We plan to extend our study to other interpretations of physical data for these systems, and we hope that this and other simple interpretations provide models for theoretical studies.

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