

Figure 4. Comparison of  $K_B$  data in  $H_2$ /bicyclohexyl with correlations.

estimated by the Riedel method using Lydersen's critical property increments (9).  $\omega$  was estimated by the Edmister method (9). The solubility parameter was estimated from the heat of vaporization calculated from the "Hildebrand rule" (7). This value is in agreement with that calculated with the Giacalone equation (9) but is lower than the value suggested by Riddick and Bunger (10). Cukor and Prausnitz (4) reported a value of solubility parameter smaller than that used in this work. The estimated physical properties of bicyclohexyl of this work are listed in Table III.

#### Glossary

$f_i$  fugacity of component  $i$ , atm

$H$  Henry's constant, atm  
 $K_i$  vaporization equilibrium ratio  $\equiv y_i/x_i$   
 $p$  pressure, atm  
 $T$  temperature, K  
 $\bar{V}$  molar volume, mL/g-mol  
 $x_i$  mole fraction of component  $i$  in liquid phase  
 $y_i$  mole fraction of component  $i$  in gas phase  
 $\delta$  solubility parameter, (cal/mL)<sup>1/2</sup>  
 $\omega$  acentric factor

#### Subscripts

H hydrogen  
 B bicyclohexyl  
 C critical properties

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## Density, Viscosity, and Surface Tension of Some Single Molten Hydrated Salts

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Viscosity and surface tension of molten  $Cr(NO_3)_3 \cdot 9H_2O$ ,  $Mn(NO_3)_2 \cdot 6H_2O$ ,  $Fe(NO_3)_3 \cdot 6H_2O$ ,  $FeCl_3 \cdot 6H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ , and  $Cd(NO_3)_2 \cdot 4H_2O$  and the density of  $Co(NO_3)_2 \cdot 6H_2O$  and  $Zn(NO_3)_2 \cdot 6H_2O$  were measured as a function of temperature. The temperature coefficient of molar surface energy (Eötvös constant) is found to depend on the molecular mass of the salt. Fluidities show non-Arrhenian behavior.  $T_0$  values computed through  $\phi = A_\phi T^{1/2} \exp(-B_\phi / (T - T_{0,\phi}))$  lie close to the experimentally determined glass-transition temperatures but fail to show the same sequential order.

Increasing interest in hydrated melts, which provide liquids involving high acidities and possessing strong supercooling and glass-forming tendencies, necessitated a systematic and multipronged physicochemical investigation of these systems.

Table I. Densities and Equivalent Volumes of Molten  $Co(NO_3)_2 \cdot 6H_2O$  and  $Zn(NO_3)_2 \cdot 6H_2O$

Temp, °C	Density, g cm <sup>-3</sup>	Equiv vol, cm <sup>3</sup> equiv <sup>-1</sup>
$Co(NO_3)_2 \cdot 6H_2O$		
44.5	1.7900	81.28
49.6	1.7849	81.51
53.0	1.7818	81.66
57.0	1.7779	81.84
64.0	1.7710	82.15
70.0	1.7653	82.42
78.8	1.7555	82.88
$Zn(NO_3)_2 \cdot 6H_2O$		
39.0	1.8256	81.46
43.0	1.8211	81.66
49.0	1.8141	81.98
57.0	1.8051	82.39
64.5	1.7965	82.78
72.2	1.7873	83.21
80.0	1.7783	83.63

Table II. Density/Equivalent Volume-Temperature Equations for  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  Melts

Salt	Temp range, °C	Data points	$\rho(\text{g cm}^{-3}) = a - bt$				$V(\text{cm}^3 \text{equiv}^{-1}) = A + Bt$				$10^4 \alpha(75^\circ \text{C}), \text{deg}^{-1}$
			$a$	$10^3 b$	$10^3 \text{SE}$	$10^3 \text{M dev}^a$	$A$	$10^2 B$	SE	$\text{M dev}^a$	
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	44-79	7	1.8345	0.995	0.37	-0.57	79.22	4.61	0.02	+0.03	5.58
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	39-80	7	1.8707	1.154	0.15	+0.23	79.39	5.29	0.01	-0.01	6.27

<sup>a</sup> Maximum departure from the best fit straight line.

Table III. Surface Tension ( $\sigma$ ) Values for Some Hydrated Melts

Temp, °C	$\sigma, \text{mN m}^{-1}$	Temp, °C	$\sigma, \text{mN m}^{-1}$	Temp, °C	$\sigma, \text{mN m}^{-1}$
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$		$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$		$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	
35.0	87.0	31.5	81.5	50.0	91.5
50.0	83.8	48.8	77.5	59.0	90.4
77.5	77.9	61.0	74.7	77.0	88.1
		73.6	71.9		
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$		$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	
45.0	96.6	31.0	95.1	50.0	91.0
60.0	94.8	40.0	93.9	63.0	89.7
81.0	91.9	50.0	92.7	76.0	88.5
		63.0	91.5		
		77.0	90.3		
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$		$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$		$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	
39.0	91.4	42.0	101.4	34.2	72.8
50.0	89.7	50.0	99.4	50.5	69.8
64.0	88.4	73.0	93.8	61.6	68.3
77.5	87.1			73.1	66.7

Recently, volumetric properties of hydrated transition metal nitrates and chlorides in the molten state have been reported (10). This communication reports the first measurement of surface tension and viscosity of molten hydrated nitrates of metals belonging to the 3D series of transition elements.

### Experimental Section

The source and the quality grade of the salts used in this study are the following:  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Ortolan (Italy), Analytical Reagent;  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Riedel (Germany), Guaranteed Reagent;  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Riedel (Germany), Guaranteed Reagent;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , BDH (India), Laboratory Reagent;  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , BDH (India), Laboratory Reagent;  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , BDH (England), Laboratory Reagent;  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , S. Merck (India), Laboratory Reagent;  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , BDH (India), AnalaR grade;  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Reanal (Hungary). The melting temperatures of these salts, determined by the cooling curve method, are included in Table V. The agreement between the experimentally measured melting temperatures and those reported in literature (14) leads one to believe that the salts were of the stoichiometry reported by the manufacturers. This, however, was verified for zinc nitrate hexahydrate by the EDTA titrimetric method (13); ferric and nickel salts were verified by standard gravimetric methods (13) and the salts of  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  by determining the loss in weight on complete dehydration at 140-150 °C. Repeated cross checks gave the water content of these salts to be within +0.03 and -0.02 of the stoichiometric values. The salts were fused

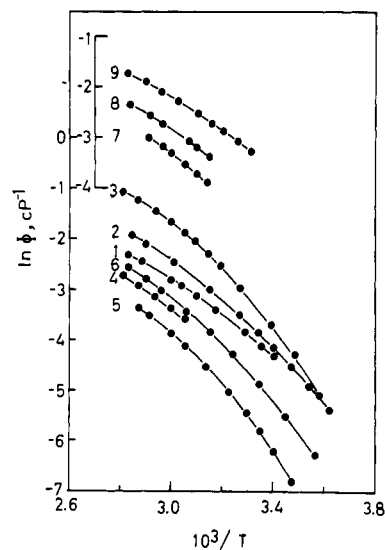


Figure 1. Plot of  $\ln(\text{fluidity})$  vs.  $T^{-1}$  for some single molten hydrates: (1)  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (2)  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , (3)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , (4)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (5)  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (6)  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , (7)  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (8)  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , (9)  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

in hard glass flasks (ca. 100 cm<sup>3</sup>) fitted with airtight ground glass joints and filtered through a sintered glass filter (porosity G-3) under a slight positive pressure of dry and  $\text{CO}_2$  free air. The filtered melts were maintained at 60-70 °C for about 1 h for maturing.

Viscosities were measured with Canon-Fenske type viscometers, calibrated with aqueous solutions of sucrose and glycerol. The viscometer constants were 0.2009 and 0.2647 cP s<sup>-1</sup>. Inherent accuracy in these measurements is estimated to be  $\pm 0.5\%$ .

Surface tensions were measured by the differential capillary rise method. A Pyrex tube (2 × 25 cm) fitted with a ground glass joint at the upper end acted as the melt container. Two precision capillary tubes of different cross section were fused to the upper joint in such a way that the lower flat ends of the capillaries were in the same horizontal plane at a depth of about 2 mm below the melt surface. Two fine holes in the upper part of the melt container helped in maintaining the inside pressure equal to the atmospheric pressure. Before each run, the apparatus was cleaned with hot chromic acid, thoroughly washed in running water, rinsed with distilled water, and dried in a dust-free electric oven. The internal radii of the capillary tubes were measured by means of a microscope (least count 0.0005 cm) and con-

Table IV. Surface Tension-Temperature ( $T$ , K) Equations and Related Parameters for Some Hydrated Melts

Salt	$\sigma(\text{mN m}^{-1}) = a - bT$			$10^2(H^\sigma/A^\sigma), \text{J m}^{-2}$	$10^4(S^\sigma/A^\sigma), \text{J m}^{-2} \text{K}^{-1}$	Eötvös constant
	$a$	$10b$	SE			
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	153.37	2.15	0.02	15.34	2.15	7.03
$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	126.63	1.04	0.18	12.66	1.04	2.05
$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	151.13	2.29	0.06	15.11	2.29	7.03
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	121.90	0.96	0.007	12.19	0.96	1.86
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	132.42	1.26	0.002	13.24	1.26	2.81
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	125.83	1.11	0.27	12.58	1.11	2.19
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	138.24	1.31	0.13	13.82	1.31	2.71
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	178.83	2.46	0.04	17.88	2.46	5.67
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	121.13	1.58	0.24	12.11	1.58	3.23

Table V. Viscosities of Some Molten Hydrated Salts<sup>a</sup>

Temp, °C	$\eta$ , P	Temp, °C	$\eta$ , P
Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, 36.9 (37 °C)			
6.5	5.4628	44.0	0.4710
11.5	3.5570	48.5	0.3878
16.0	2.5184	53.5	0.3155
20.8	1.7962	59.0	0.2543
25.8	1.3054	65.0	0.2051
31.6	0.8891	72.0	0.1644
35.5	0.7186	80.5	0.1273
39.7	0.5802		
Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, 26.0 (25.8 °C)			
21.0	0.7474	50.0	0.2287
25.2	0.6134	56.0	0.1896
31.0	0.4651	60.0	0.1679
32.0	0.4515	67.5	0.1376
42.0	0.3017	73.5	0.1180
46.0	0.2606	80.0	0.1017
Fe(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O, 35.0 (35.0 °C)			
2.5	2.2974	44.5	0.2002
5.0	1.8892	48.5	0.1708
9.0	1.3787	54.0	0.1406
14.5	0.9433	59.0	0.1186
21.0	0.6283	65.0	0.0982
26.0	0.4772	71.0	0.0829
32.8	0.3367	78.0	0.0685
39.5	0.2480		
FeCl <sub>3</sub> ·6H <sub>2</sub> O, 36.9 (37.0 °C)			
5.4	1.6478	50.0	0.0778
14.0	0.7449	54.0	0.0662
21.5	0.4080	60.0	0.0539
32.3	0.1957	67.5	0.0423
40.0	0.1265	75.5	0.0347
44.5	0.1001	82.5	0.0294
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, 54.7			
44.5	0.2938	64.0	0.1551
49.6	0.2452	70.0	0.1327
53.0	0.2188	78.8	0.1055
57.0	0.1920		
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, 56.8 (56.7 °C)			
54.0	0.3598	75.5	0.1877
60.0	0.2939	82.5	0.1528
67.5	0.2329		
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, 36.9 (37 °C)			
28.8	0.2673	57.0	0.0990
33.5	0.2190	64.5	0.0808
39.0	0.1782	72.2	0.0671
43.0	0.1544	80.0	0.0572
49.0	0.1261		
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, 42.7 (42.7 °C)			
14.5	9.2595	49.0	0.7888
21.0	5.0730	54.0	0.6218
26.0	3.3041	60.0	0.4875
30.5	2.3626	64.0	0.4170
37.0	1.5215	70.0	0.3337
45.5	0.9420	74.5	0.2880
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, 59.4 (59.4 °C)			
45.5	0.4874	64.0	0.2413
49.0	0.4192	70.0	0.1985
54.0	0.3430	74.5	0.1741
60.0	0.2756		

<sup>a</sup> Values in parentheses are the literature (14) melting temperatures.

firmed by calibrating with distilled mercury; these were estimated to be 0.0265 and 0.0465 cm. The melts were held at a depth of about 15 cm from the free surface of the oil in the constant temperature bath. Under the conditions of thermal equilibrium, the temperature did not vary by more than  $\pm 0.1$  °C over the region of interest. The difference in the levels of a liquid in the two capillaries was measured with a precision of  $\pm 0.001$  cm.

The experimental surface tension values are expected to be accurate to  $\pm 0.25$  mN m<sup>-1</sup>.

Densities of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O determined by measuring the volumes of a known amount of melt, in a manner described earlier (9) are precise to  $\pm 0.1\%$ . A liquid paraffin bath (ca. 15 L) was employed as the constant temperature bath, whose temperatures were controlled and measured with a precision of  $\pm 0.1$  °C.

## Results and Discussion

**Densities and Equivalent Volumes.** Densities and equivalent volumes of cobalt and zinc nitrate hexahydrates, in the molten state at various temperatures are presented in Table I. The data could be satisfactorily described by the equations

$$\rho(\text{g cm}^{-3}) = a - bt \quad (1)$$

and

$$V(\text{cm}^3 \text{equiv}^{-1}) = A + Bt \quad (2)$$

The coefficients  $a$ ,  $b$ ,  $A$ , and  $B$  are recorded in Table II. Expansivities ( $\alpha$ ) of the melts expressed as

$$\alpha = (1/V)(dV/dT)_P \quad (3)$$

are also included in Table II. The computed equivalent volumes of these salts support the earlier observation (10) that the hydrated salts having the same number of moles of water of hydration per equivalent of the cationic charge appear to have almost equal equivalent volumes, irrespective of the total charges on the cation and its radius. For salts having this ratio equal to 3, the volumes (at 75 °C) were found to be  $82 \pm 2$  cm<sup>3</sup> equiv<sup>-1</sup>. The question how this ratio determines the packing density of these liquids could not be rationalized as yet.

**Surface Tension.** The surface tension ( $\sigma$ ) values for all the salts at various temperatures are presented in Table III. The corresponding least-squares fits are recorded in Table IV. Eötvös constants evaluated from the least-squares fit of  $\sigma(M/\rho)^{2/3}$ -temperature ( $T$ , K) data, are also included in Table IV. These are found to be of the same order as that observed for normal liquids and appear to be governed by molecular mass of the salt. If, this mass dependence of Eötvös constant is correct, then relatively much smaller values (0.5–1) of this constant for certain molten halides as reported by Bloom et al. (5) are not unrealistic in view of their high degree of dissociation in the molten state. Since, the surface tension of a liquid is defined as its surface free energy per units area, the surface entropy ( $S^\sigma/A^\sigma$ ) and the surface enthalpy ( $H^\sigma/A^\sigma$ ) per unit area are given by

$$S^\sigma/A^\sigma = -d\sigma/dT \quad (4)$$

$$H^\sigma/A^\sigma = \sigma - T(d\sigma/dT) \quad (5)$$

As the temperature coefficient of surface tension is constant, for any liquid, the quantity  $H^\sigma/A^\sigma$  would be constant and independent of temperature. In view of this and the fundamental nature of the quantity, it may thus be used to compare different molten hydrated salts. These calculated quantities have been included in Table IV. The  $S^\sigma/A^\sigma$  values are much higher than those reported for molten salts (5) but lie close to the corresponding values for aqueous solutions of electrolytes. This indicates that the surface properties of the liquids reported in this communication are influenced by electrostricted dipoles of the coordinated water.  $H^\sigma/A^\sigma$  values place these liquids somewhere between anhydrous molten salts having  $H^\sigma/A^\sigma$  values ranging between 0.2 and 0.15 J m<sup>-2</sup> and the nonpolar,

Table VI. Parameters of the Equation,  $\phi = A_\phi T^{-1/2} \exp(-B_\phi/(T - T_{0,\phi}))$  Computed for the Fluidity-Temperature Data of Some Molten Hydrated Salts

Salt	Cation radius, Å	Temp range, °C	Data points	$A_\phi$ , cP <sup>-1</sup>	$B_\phi$ , K	$T_{0,\phi}$ , K	$10^3SE$ , cP <sup>-1</sup>	$T_g$ , K	For $B = 675$ K		
									$A_\phi$ , cP <sup>-1</sup>	$T_{0,\phi}$ , K	$10^3SE$ , cP <sup>-1</sup>
Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	0.69	6-80	15	219.43	844.91	184.63	0.16	208	106.95	197.47	0.86
Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.80	21-80	12	126.31	752.60	175.02	0.11	191	95.91	182.56	0.26
Fe(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	0.64	3-78	15	293.51	806.56	178.67	0.16	240	171.29	189.15	1.24
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.74	45-79	7	190.77	858.61	168.41	0.18	206	105.88	187.05	0.27
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.72	54-82	5	1957.03	1950.07	91.23	0.31	210	78.58	193.72	0.53
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.74	29-80	9	142.58	638.43	183.60	0.44	197	161.99	179.66	0.54
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0.99	14-75	12	63.72	628.74	210.68	0.06	218	79.47	207.08	0.14
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0.97	45-75	7	115.94	729.21	192.02	0.06	211	95.20	197.31	0.07
FeCl <sub>3</sub> ·6H <sub>2</sub> O	0.64	6-82	12	324.14	574.66	207.71	4.9	203	520.73	199.61	8.71

Table VII. Comparison of Parameters of Equation 6 for Conductance and Fluidity Data of Molten Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O

Ref	$T_{0,\phi}$ , K	$T_{0,\Delta}$ , K	$B_\phi$ , K	$B_{\Delta}$ , K	$A_\phi$ , cP <sup>-1</sup>	$A_{\Delta}$ , S cm <sup>2</sup> equiv <sup>-1</sup>
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O						
Present study	210.68		628.74		63.72	
	207.08		675.0		79.47	
12	203.8	199.8	676.51	625.12	84.28	3600
3 <sup>a</sup>	210	202	665	620	80	3500
11	207		633.2			
7	205.5	203.4	671.16	542.53	85.80	2120
8	206.9	206.0	700.63	523.31	120.37	1975.8
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O						
Present study	192.02		729.21		115.94	
	197.31		675.0		95.20	
12	205.5	194.5	554.07	587.86	64.10	3825

<sup>a</sup> Estimated from Figure 6.

room temperature liquids for which the corresponding values lie between 0.04 and 0.07 J m<sup>-2</sup>.

**Viscosity.** Table V records the experimentally determined viscosities for all the salts investigated in this study. In  $\phi$  vs.  $T^{-1}$  plots (Figure 1) showed significant curvature, exhibiting the non-Arrhenian behavior shown by these salts. The fluidity  $\phi$  ( $=\eta^{-1}$ )-temperature data were processed on an IBM 360/44 data processing system to fit into expression 6, by an iterative

$$\phi = A_\phi T^{-1/2} \exp(-B_\phi/(T - T_{0,\phi})) \quad (6)$$

method, where  $A_\phi$ ,  $B_\phi$ , and  $T_{0,\phi}$  are constants characteristic of the system. The constant  $T_{0,\phi}$  in this expression represents the temperature at which ionic mobilities fall to zero and has been shown to be of thermodynamic significance by Cohen and Turnbull (6), Adam and Gibbs (1), and Angell and Rao (4). Refinement in the values of the parameters  $A_\phi$ ,  $B_\phi$ , and  $T_{0,\phi}$  was carried out until the two successive values of these parameters did not differ by more than  $\pm 0.01$ . However, for the fluidity data of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, the last correction term for the exponential coefficient ( $B_\phi$ ) could not be bettered beyond 0.09. Since the single salt melts except those of trivalent metal ions did not show significant supercooling, the measurements could not be extended much below their melting temperatures. This constraint was reflected in poor parallelism between estimated  $T_{0,\phi}$ 's and the experimentally determined glass-transition temperatures ( $T_g$ 's); the latter were estimated from the work of Angell and Sare (2). Inspection of the best fit parameters in Table VI does not reveal any systematic trend in  $A_\phi$ ,  $B_\phi$ , and  $T_{0,\phi}$  values. This is because of strong interdependence of these

parameters, so that if the data do not cover a reasonably extensive range, one can find a number of  $A_\phi$ - $B_\phi$ - $T_{0,\phi}$  sets which could describe the system equally well. Small changes in  $T_{0,\phi}$  will produce much larger changes in  $A_\phi$  and  $B_\phi$ . To seek a meaningful correlation between  $T_{0,\phi}$ 's and  $A_\phi$ 's with the basic parameters of the ions constituting the salts, the fluidity data were processed to fit into eq 6 at a constant value of 675 K for  $B_\phi$  (cf. Moynihan et al. (12)). This, however, resulted in a slight increase in the standard deviation of the fits relative to the best-fit standard deviations. The computed parameters are presented in Table VI. The effect of an individual cation on  $T_{0,\phi}$ 's is not defined. This could be because of the fact that the cations are shielded behind one or two sheath(s) of tightly held water molecules and thus present essentially a similar exterior.

A cursory inspection of  $A_\phi$  values (Table VI) reveal that these salts can be classified into three sets. The first includes the salts of trivalent chromium and iron; the salts of Mn<sup>2+</sup>, Co<sup>2+</sup>, and Zn<sup>2+</sup> fall into a second while those of Ca<sup>2+</sup> and Cd<sup>2+</sup> fall into a third. In each set of salts having cations of almost equal size,  $A_\phi$ 's show a direct dependence on the cationic mass, a trend in the reverse direction to that predicted by the theory (6). A similar observation reported by Moynihan et al. (12) for the system containing tetrahydrates of calcium and cadmium nitrates has been interpreted as a reflection of differences in the lability of water or nitrate ions in the coordination shells of the cations. In Table VII, a facial comparison of the parameters  $A$ ,  $B$ , and  $T_0$  reported by various workers from their conductivity and fluidity results for molten tetrahydrates of calcium and cadmium nitrates has been made.

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