

TRANSPORT PROPERTIES OF MOLTEN HYDRATED SALTS

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Density, conductivity and viscosity measurements in molten calcium and cadmium nitrate tetrahydrates and zinc and magnesium nitrate hexahydrates with some monovalent (Li, Na, K, Rb, Cs, Ag, Tl and NH_4) nitrates have been made in the available temperature and composition range. The temperature-dependence of density and equivalent volumes were found to be linear. Equivalent volumes-equivalent fraction of monovalent nitrate isotherms were linear. The principle of additivity of volumes was obeyed except in presence of LiNO_3 where deviations have been explained in terms of hydration-dehydration equilibrium.

The non-arrhenius temperature dependence of conductivity and fluidity has been interpreted in terms of Vogel-Tammann-Fulcher equation and the environmental relaxation model of liquid transport; the composition dependence of the variables has been discussed considering structural (free volume) and thermodynamic (configurational entropy) parameters of the liquids. Conductivity/fluidity vs volume data obeyed Doolittle equation. Composition variation of conductivity and fluidity has been interpreted in terms of anion polarisation model and Kendall equation respectively in conjunction with the tendency of cations to be preferentially hydrated.

Keywords : Transport; Molten Hydrated Salts; Non-Arrhenius Temperature Dependence; Doolittle Equation; Anion Polarisation Model; Kendall Equation; Vogel-Tammann-Fulcher Equation

INTRODUCTION

THE study of low temperature molten salt systems has been currently receiving the attention of several investigators. These systems consist of highly concentrated aqueous electrolyte solutions, molten hydrated salts and anhydrous molten binary/ternary systems with deep eutectic. These systems possess low liquidus temperature, good solvent behaviour, high electrical and thermal conductivity, and often supercooling and glassforming tendencies. Several of these systems are of intrinsic chemical and industrial importance and are finding use in thermal and electrochemical energy storage systems, fuel cells, hydrogen production, geothermal brines, heat exchanger in reactors and low temperature protonic semiconductors. In this paper, the results of density, conductivity and viscosity measurements of the molten hydrates of calcium, cadmium, zinc and magnesium nitrate with Li, Na, K, Rb, Cs, Ag, Tl, NH_4 -nitrate, over wide temperature and composition range, have been

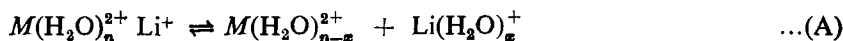
analysed using different transport models of liquid. The experimental details have been described earlier (Gaur & Jain, 1971, 1972; Sharma & Gaur, 1976, 1977a, b; Sharma *et al.*, 1978, 1979a, b; and Sunita Gupta *et al.* — *In Press*).

RESULTS AND DISCUSSION

Density and Equivalent Volume

Temperature Dependence—Data of densities of the molten mixtures of divalent cationic hydrates with monovalent nitrates were available over a wide composition region at temperatures between 288.2 to 363.2 K. Equivalent volumes were calculated using mass of the mixtures containing 1 mol of NO_3^- ions; 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 volume with composition would reflect directly the changes in the packing density. Equivalent volumes and densities varied linearly with temperature. The equivalent volume of the systems was found to be directly proportional to the van der Waals volumes and decreased with increase in monovalent nitrate content. This appeared logical as the larger hydrated cations — $\text{Ca}(\text{H}_2\text{O})_4^{2+}$, $\text{Cd}(\text{H}_2\text{O})_4^{2+}$, $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Mg}(\text{H}_2\text{O})_6^{2+}$, whose presence have been demonstrated by spectral and allied measurements (Angell, 1964; Hester & Plane, 1964; Moynihan *et al.*, 1966; Braunstein & MacDonald, 1967; and Irish & Davis, 1968) are replaced by relatively smaller cations in per equivalent unit.

Composition Dependence — Equivalent volume vs equivalent fraction isotherms were linear except for LiNO_3 -containing systems. The linearity of the plots indicated the applicability of the principle of additivity of volumes. Partial equivalent volumes of the components were in good agreement with the volumes of pure components. The anomalous behaviour of Li^+ containing systems could be explained in terms of greater hydrophilic tendency and capacity of Li^+ ions to decoordinate water molecules from the hydration sheath of divalent cations as follows :



The increased size of Li^+ ions because of hydration would unbalance the packing, resulting positive or negative deviations from linearity depending on the quantity of water associated with the systems.

Conductivity and Viscosity

Composition Dependence — Conductivity (λ) of the mixtures increases non-linearly with increase in MNO_3 content (Fig. 1) except for LiNO_3 — containing mixtures. The results could be explained in terms of anion polarisation model (Moynihan & Laity, 1964) based on physical interactions among the ions. The NO_3^- ion is subjected to different magnitudes of ionic interactions in the environment of divalent hydrated and monovalent cations. The preferential orientation of NO_3^- ions towards

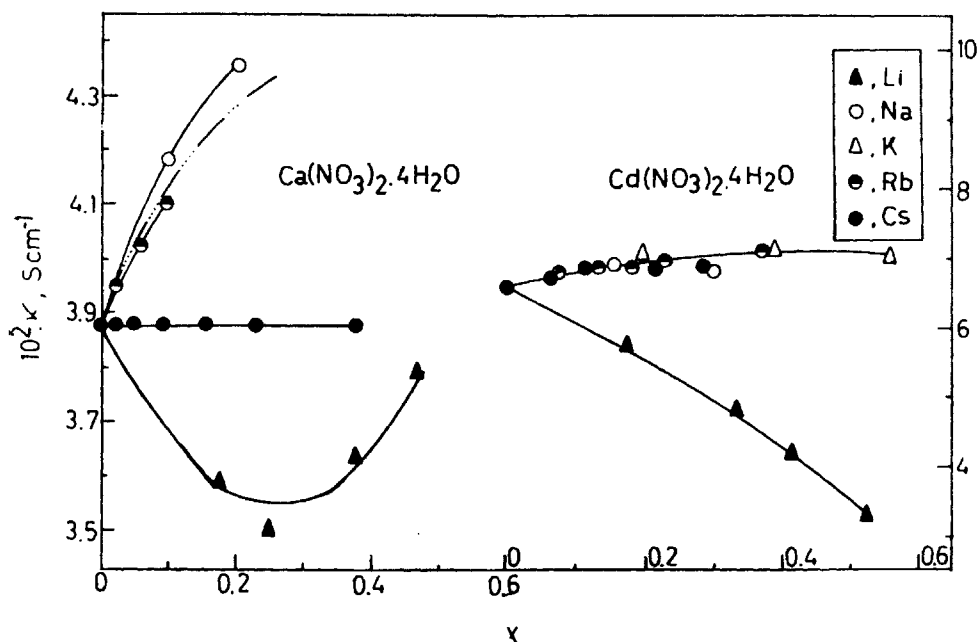


FIG. 1. Conductivity (κ) vs. mole fraction of $\text{MnO}_3(X)$ isotherms at 323.2K.

monovalent cations because of its high cationic potential enhance the mobility of hydrated divalent cations in the system. A nonsystematic variation in LiNO_3 containing mixtures may be due to preferential hydration of Li^{+3} ions. This would lead to dehydration of cations or an equilibrium as represented by (A). Fluidity composition isotherms were linear indicating applicability of Kendall equation.

Temperature Dependence — The Arrhenius plots of conductivity and fluidity (not shown) were curved in a direction such that decrease in temperature increases the activation energy, indicating that ionic movement ceases at a temperature higher than 0°K . The $(\Lambda, \Phi) - T$ data were iterated using Simplex II method in Vogel-Tammann-Fulcher equation (Vogel, 1921; Fulcher, 1925; and Tamman & Haase, 1926).

$$\Lambda, \Phi = A1 \exp\left(-\frac{B1}{T - T_0}\right) \quad \dots(1)$$

and in the equations based on free volume model (Cohen & Turnbull, 1959)

$$\Lambda, \Phi = A2 T^{-1/2} \exp\left(-\frac{B2}{T - T_0}\right) \quad \dots(2)$$

and configurational entropy model (Adams & Gibbs, 1965)

$$\Lambda, \Phi = A3 T^{-1/2} \exp\left(-\frac{B3}{T \ln T/T_0}\right) \quad \dots(3)$$

The reliability of computer evaluation of the parameters of eqns. (1), (2) & (3) was supported by the linearity of $\ln(\Lambda, \Phi)$ vs $(T - T_0)^{-1}$, $\ln(\Lambda, \Phi) T^{1/2}$ vs $(T - T_0)^{-1}$ and $\ln(\Lambda, \Phi) T^{1/2}$ vs $(T \ln T/T_0)^{-1}$ plots.

Composition-Dependence of A_Δ 's, B_Δ 's and T_0 's—Composition variation of A_Δ , B_Δ and T_0 are shown in Fig. 2. There is no systematic variation in the A_Δ which according to FVM should have a dependence of the type, on mass and radius of

$$A_\Delta \propto m^{1/2}/r \quad \dots(4)$$

on mass and radius of the particles being transported. In ionic systems, the composition variation of A_Δ require a more appropriate formulation in terms of mass and radius of ions. However, it has been observed that A_Δ obeyed the relation (4) when B_Δ is kept constant for the mixtures. The coefficient B_Δ exhibited a decrease with increasing MNO_3 content. The B_Δ is a measure of energy barriers which an ion has to cross before transport process took place. The examination of B_Δ values revealed that the distribution of free volume in ionic systems was non-random.

The ideal glass transition temperature, T_0 , exhibited an increase with the addition of monovalent nitrates. T_0 is a useful parameter to measure the interaction energy between the bulk species of the systems. In molten hydrated salts and highly

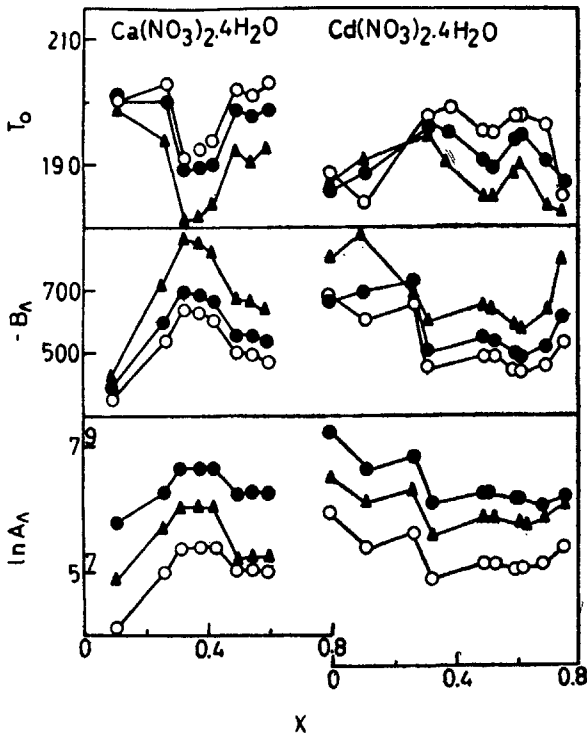


FIG. 2. Composition dependence of the parameters of VTF, FVM & CRT for conductance data of $M(NO_3)_2 \cdot 4H_2O + NH_4NO_3$ systems.

concentrated aqueous electrolyte solutions, the total interaction energy would be contributed by ion-ion, ion-water and water-water interactions, that due to ion-water interaction would predominate. The addition of MNO_3 to hydrated melts, though increase the coulombic energy of the system, an examination of T_0 reveal that total cohesive energy of the systems remained almost constant except in mixtures containing $LiNO_3$. A direct consequence of this is seen in $\sum \frac{n_i z_i}{r_i}$ vs. T_0 plots (Fig. 3) which indicated that the points are closely surrounded around cationic potential of ~ 0.5 . An extrapolation of these plots reveal that for systems having cationic potentials zero, the T_0 is in good agreement with the glass transition temperatures of water and other molecular liquids.

Conductivity/Fluidity-Volume Data : The conductivity/fluidity vs. volume data did not obey (Hildebrand, 1971) equation. The parameters of Doolittle (1951) equation,

$$\Lambda, \Phi = A4 \exp \left(- \frac{B4}{V - V_0} \right) \quad \dots(5)$$

were evaluated and applicability of this equation is established by the linearity of $\ln \Lambda, \Phi$ vs. $(V - V_0)^{-1}$ plots. A good agreement in $V_{0,\Lambda}$ & $V_{0,\Phi}$ and a parallelism of V_0 values with the volumes at T_0 support the usefulness of eqn. (5) to describe transport data.

The Environmental Relaxation Model : Conductivity and fluidity data have also been processed using the semiempirical relation of environmental relaxation model (Simmons & Macedo, 1971)

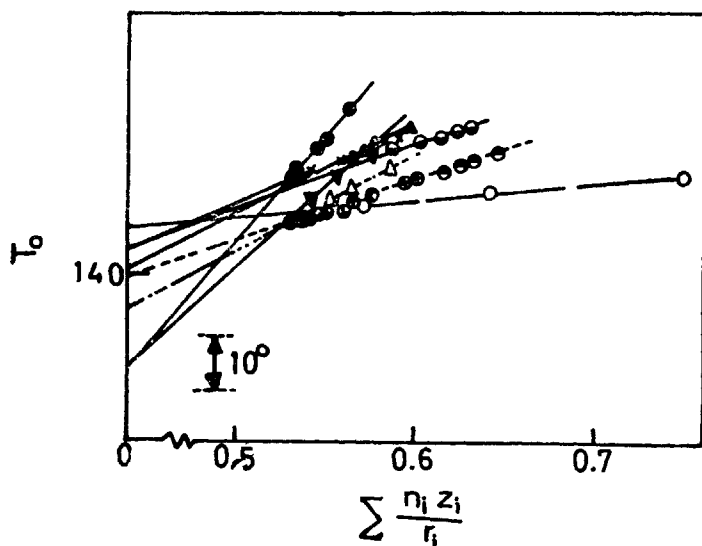


FIG. 3. Dependence of T_0 on cationic potential $\sum n_i z_i / r_i$.

$$-\ln \Lambda = \ln AG_{\infty} + \frac{\hat{B}}{RT} + \frac{C_0}{2RT} \left[\frac{T_0^4}{T_0^4 + \epsilon_0^2 (T - T_0)^4} \right]^{3/2} \quad \dots(6)$$

to test its applicability to the present data. Though small temperature range data did not allow an unambiguous evaluation of the parameters of eqn. (6), being its highly inter-dependent an attempt has been made applying conditional approach. Since T_0 is the temperature at which the magnitude of transport properties reduces to zero, it will be a constant for a particular chemical system and independent of transport process. The T_0 evaluated using FV, CR or ERM model will thus be the same. The values of parameters of the equation 6 are evaluated by iteration method keeping T_0 constant and adopting its value from FV or CR model. Linearity of $-T \ln AG_{\infty} (\Lambda, \Phi)$ vs. $[T_0^4 / \{T_0^4 - \epsilon_0^2 \times (T - T_0)^4\}]^{-3/2}$ (not shown) establish the applicability of equation 6 to transport data.

Variation of parameters of ERM with composition are shown in Fig. 4. The parameter $\ln (AG_{\infty})$ is the product of frequency factor of Eyring rate equation and instantaneous shear modulus. A non-systematic variation in $\ln (AG_{\infty})$ is obtained from Λ - T and Φ - T fitting of data in equation 6. Since frequency factor A

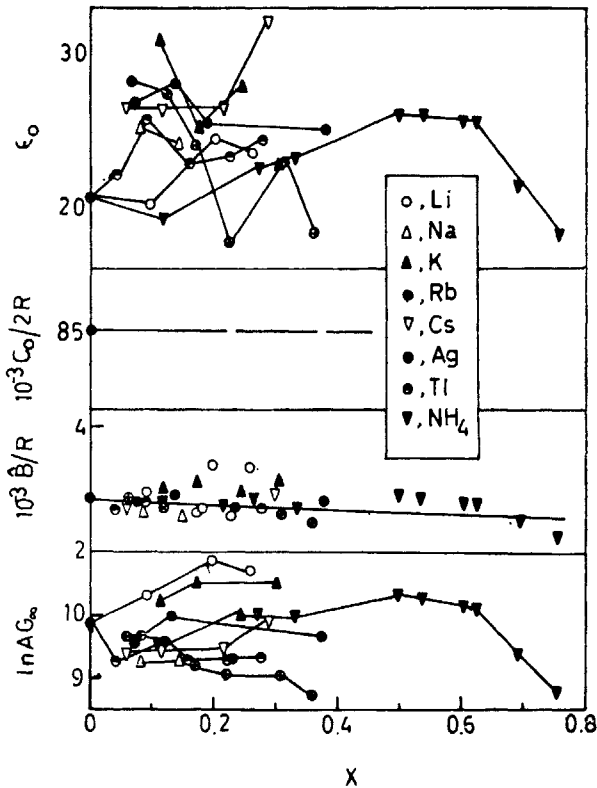


FIG. 4. Composition dependence of the parameters of ERM for conductance data of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{MnO}_3$ systems.

from FVM exhibit a similar variation, it can be however concluded that the instantaneous shear modulus of these systems remains almost constant.

The parameter \hat{B} is average activation energy around which the Gaussian distribution of activation energy takes place. Variation of \hat{B} exhibit a decreasing trend with increasing MNO_3 content except for LiNO_3 . This indicates that average energy of activation decreases with the addition of monovalent nitrates. Comparison of \hat{B}_Λ and \hat{B}_Θ exhibit their ratios to be $B_\Theta/B_\Lambda = 1.1$, indicating that average activity energy for viscosity is higher than that of conductivity.

The parameter C_0 have been found constant for both the conductivity and fluidity. In molten anhydrous salts it was concluded from dielectric relaxation measurements (Bose *et al.*, 1970) that the relaxing species contributing to conductivity were the cations while anions were relaxing species for viscous flow. The C_0 is the low temperature limit of activation energy. Constancy of C_0 in the whole concentration region thus reveals that activation energy of these mixtures converge to the same point for the low temperatures. However, the different relaxing species for different transport processes will result in different structural interactions which predict that,

$$C_{0,\Lambda} = C_{0,\Theta}/q^3 \quad \dots(7)$$

where q is a constant and its value for molten anhydrous salts was found to be 1.18 while for our systems it is unity. This indicates that low temperature limit of activation energy for conduction and flow processes must be same. This, however, cannot be taken as true. The constancy of C in present systems might be due to a small temperature range available which might not result a true value of low temperature activation energy limit as expected from extended low temperature region data.

ϵ_0 which relates the size of microstructure to range of interactions was found almost constant for the system and its value was found to be 22 ± 5 . For concentrated solutions on which work is in progress in this laboratory, the value of ϵ_0 ranges between 5–30. It has been considered that in non-Arrhenius region, the size of microstructure is of the same order as the range of structural interactions. For a particular composition, range of interaction will be the same and size of microstructure increases as temperature decreases. The low temperature data will provide a limiting value of ϵ_0 which will be characteristic of chemical system. The ratio of $\epsilon_{0,\Lambda}$ and $\epsilon_{0,\Theta}$ was also found to be unity while ERM suggest

$$\epsilon_{0,\Lambda} = \epsilon_{0,\Theta}/q^3 \quad \dots(8)$$

The low value of q may be considered to arise due to a small temperature range available for the study.

Although, ERM formulations are widely applicable to explain the transport behaviour of ionic liquids, the evaluated parameter from a short range data will not provide the ideal value. In a short temperature range, non-Arrhenius behaviour of transport properties can be better explained by CRT formulations.

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Discussion

- A. V. GORODYSKY (*Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, USSR*): (i) Have you some diffraction or spectroscopic data about mixed molten hydrates? (ii) What is the contribution of each ions to conductivity? (iii) To what extent the water is dissociated?
- H. C. GAUR: (i) The spectral data on mixed molten hydrates particularly in presence of LiNO_3 , where interesting results of hydration-dehydration are expected, are in progress. (ii) It varies. (iii) Almost undissociated.