SUMMARY
In Chapter I density and viscosity measurements of six aqueous solutions, viz., \( \text{Ca(NO}_3\text{)}_2\cdot\text{H}_2\text{O}, \text{Mg(NO}_3\text{)}_2\cdot\text{H}_2\text{O}, \text{MgCl}_2\cdot\text{H}_2\text{O}, \text{NiCl}_2\cdot\text{H}_2\text{O}, \text{Na}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}, \text{and NaNO}_3\cdot\text{H}_2\text{O} \) were made as functions of temperature and concentration. The concentration was varied from low value up to nearly the concentration of saturation (saturation point) of each solute in water at room temperature (~20°C). Density has been found to be linear functions of temperature and molar concentration, but varies non-linearly with molal concentration. The non-Arrhenius temperature dependence of viscosity has been analyzed in terms of the three-parameter Vogel-Tammann-Fulcher (VTF) equation. In each electrolytic solution the ideal glass transition temperature, one of the parameters of the VTF equation, has been found to vary linearly with the molal concentration. Such a variation of \( T_0 \) with concentration has been attributed to the ion-solvent interactions (hydration) taking place within the electrolytic solution. Quantitative expressions have been obtained to account for the concentration dependences of the other two parameters of the VTF equation by introducing the empirical temperature dependence of heat capacity in the Adam-Gibbs equation for transport property. A three-parameter
isothermal equation has been derived from the VTF equation by substituting in it the concentration dependences of its three parameters. This isothermal equation has been found to be successful in explaining the concentration dependence of viscosity of electrolytic solutions in the entire experimental range of concentration. Other expressions used in the literature for describing the concentration dependence of viscosity have been shown to be the special cases of the newly derived isothermal equation. In each electrolytic solution studied a structural transition appears to take place at some critical concentration the value of which depends upon the system considered.

In Chapter II the conductances of the above six electrolytic solutions were measured as functions of temperature and concentration. The experimental range of concentration was the same as in the case of viscosity study. The temperature dependence of equivalent conductance has been described by the VTF equation. A three-parameter isothermal equation similar to that used in the case of viscosity describes the concentration dependence of equivalent conductance in the experimental range of concentration. Specific conductance isotherms of all the solutions studied pass
through maxima. The value of the concentration \( m_{\text{max}} \) at which the conductivity of an electrolytic solution becomes maximum has been found to be obtainable from the three-parameter isothermal equation also. An attempt has been made to correlate the \( m_{\text{max}} \) value of an electrolytic solution with the hydration number of its solute. The activation energies for conductance and viscous flows were calculated. Both the activation energy isotherms appear to pass through broad minima. The Walden product isotherm of each solution has also been found to pass through a minimum. A three-parameter isothermal equation has been obtained for describing the concentration dependence of the Walden product and this equation satisfactorily accounts for the minima observed in the Walden product isotherms. However, at low concentrations deviation from this isothermal equation has been observed. The necessity of taking into account the ion-ion interactions also, especially at low concentrations, has been highlighted. The conductance study also envisaged the occurrence of a structural transition at some concentration in the case of each electrolytic solution. This transition appears to take place over a concentration range instead of occurring at a definite concentration. The transition has
been speculated to be a change-over from a primitive structure to a quasi-crystalline structure.

The analyses of the concentration dependences of viscosity and conductances of the six electrolytic solutions under consideration were improved in Chapter III by incorporating in the above mentioned three-parameter isothermal equations the contributions to transport property from ion-ion interactions also. The measurements of density, viscosity, and conductance of the six solutions were extended to still lower concentrations. The modified isothermal equations have been found to be applicable in the concentration range from the extended low value up to the saturation point. From the improved isothermal equation for conductance the equivalent conductance of each solution at infinite dilution has been estimated fairly accurately. An improved isothermal equation has also been obtained for describing the variations in the Walden product with concentration which has been found to reproduce satisfactorily the values of the Walden product of all the solutions under consideration at low as well as high concentrations. An attempt has been made to correlate this isothermal equation for the Walden product with the Wishaw-Stokes equation. Such a correlation enabled us to estimate the ion-size parameter for the different aqueous
systems. In the case of NaNO₃ solution the calculated value of the ion-size parameter was found to be comparable with the reported value whereas in the rest of the solutions meaningful values were obtained for this parameter.

In Chapter IV it has been shown that in molten salt systems also the VTF equation may be derived by introducing in the Adam-Gibbs equation the empirical nature of the temperature dependence of heat capacity of molten salts. Such a derivation of the VTF equation provided an expression for describing the concentration dependence of its preexponential parameter in molten salt systems. The validity of this equation has been justified by using it successfully to explain the concentration dependences of the reported pre-exponential parameters for several binary molten mixtures containing hydrated salts. This expression, however, failed to explain the concentration dependence of the preexponential parameter reported for the molten mixture of calcium nitrate tetrahydrate and potassium thiocyanate. In order to find a plausible explanation for such an unexpected behaviour of this molten mixture, its density measurement was made as functions of temperature and composition. The analysis of the density data revealed that in this particular molten mixture the intrinsic volume is the key parameter and controls the
properties of the melt. This observation also provided an explanation for the unusual behaviour of the preexponential parameter of the VTF equation in calcium nitrate tetrahydrate and potassium thiocyanate melt. A two-parameter isothermal equation has been obtained for describing the concentration dependence of transport properties of binary melts. The applicability of this equation has been verified using the reported fluidity and conductance data for several melts containing hydrated salts.

In the last chapter of the thesis, Chapter V, density, viscosity, and conductivity of molten $0.3 \left[ x \text{KSCN} - (1-x) \text{NaSCN} \right] - 0.7 \text{Ca(NO}_3\text{)}_2 \cdot 4.06 \text{H}_2\text{O}$ system were measured as functions of temperature and composition with a view to examine the presence of mixed-alkali effect. The temperature dependence of fluidity and conductivity has been described in terms of the VTF equation. Mixed-alkali effect has been observed for fluidity and conductivity at relatively higher temperatures. A three-parameter isothermal equation similar to that employed in aqueous solutions has been successfully used for the first time to represent the concentration dependence of fluidity and conductivity of ternary systems exhibiting the mixed-alkali effect. The mixed-alkali
effect for conductivity has also been found to exist at isofluidity condition. The time-scale for detecting the mixed-alkali effect appears to depend upon the system under interest unlike the universal time-scale criterion suggested by others. A probable mechanistic interpretation has been given to the observed mixed-alkali effect. This interpretation is based on the view that the paired-cations form the mobile species and the concentration of such species appears to govern the conductivity of the ternary system studied.