CHAPTER-V

SUMMARY

VISCOSITY STUDIES OF SOME ELECTROLYTE SOLUTIONS IN MIXED MEDIA :

The viscosity of electrolyte solutions is a question of considerable industrual importance. The viscosity of electrolyte solutions is studied in different conditions such as temperature variation, change of concentration of electrolytes, change of concentration of solvents. Among many organic compounds, alcohols, stand out in virtue of their high solubility in water but their aqueous solutions often show abnormalities in properties, such as viscosity-composition maxima, or negative relative partial molar volumes, which are yet inadequately understood. The present work deals with study of viscosity of Barium nitrate and Calcium nitrate in methanol-water solutions.

In chapter I a brief survey of earlier work on various systems is given. The application of various equations such as Jones-Dole equation, Vand equation, Moulik equation, Thomas equation is discussed. A survey of study of various electrolytes in dioxane-water, methanol-water, water-pyridine, water-γ-picoline, water-tert butyl alcohol mixtures at different temperatures is taken. Scope of the present work is also discussed in brief.

Chapter II deals with the experimental methods adopted for the present study. Preparation of solutions is described. Ubbelohde type viscometer and ostwald modification of sprengel type pyknometer is used to determine viscosity and density respectively. Method of

determination of viscosity and density with its precautions have been given in detail.

Results on the study of viscosity of Barium nitrate in methanol-water solutions are given in chapter-III. These include the determination of viscosity of the solution with respect to effect of change in concentration of electrolyte, the effect of methanol concentration and the effect of temperature. It is observed that viscosity (η) and relative viscosity (ηr) increase with concentration of Barium nitrate, but fluidity decreases. At a given temperature and for a certain concentration of Barium nitrate the viscosity (η) and relative viscosity (ηr) increase as preportion of methyl alcohol increases, but the fluidity (ϕ) decreases. The applicablility of Jones-Dole equation, Vand equation, Thomas equation, Moulik equation is discussed. The results show that Jones-Dole equation is applicable for Barium nitrate in the concentration range studied i.e. 0.02-0.15 M value of A is very small and sometiemes negative indicting very weak ion-ion or solute-solute interaction. B coefficients are all positive but small in magnitude and decreases with increase in temperature as well as with increase in methanol content at a particular temperature. The value of dB/dT is negative therefore Barium nitrate behaves as a sturcture maker/promoter. The B coefficient becomes smaller and smaller with the increase in methanol content in the medium Vand equation is valid in the concentration range 0.06-0.15 M. The viscosity parameteres $\bar{V}$ and θ both increase with temperature and methanol

concentration. This may be ascribed to the increase in the electrostatic attraction between water dipole and the ion as large number of water molecules become available in the cosphere of the ions due to thermal agitation. The values of $\bar{V}$ of Barium nitrate increases because the ions get more and more hydrated in the presence of methanol. Barium nitrate promotes the solvent structure around ion indicating that Barium nitrate is structure-maker. Ba^{++} is electrostrictive structure-making ion with positive ionic volume ($\bar{V}_{\pm}$), hydration number (NB) and entropy change (ΔS^{*}). Moulik equation is not valid for Barium nitrate below 0.1 M concentration. The viscosity parameter 'M' increases with increase in temperature and concentration of methyl alcohol. The constant K' decreases with increase in temperature and concentration of methyl alcohol. Thomas equation is invalid for Barium nitrate in the concentration range 0.02 - 0.15 M.

The activation of parameters ΔE^{*}, ΔS^{*} and ΔF^{*} of viscous flow of solutions of Barium nitrate are more than those of solvent. It clearly indicates that there is little solute-solvent interaction. Also it indicates structure making effect of Barium nitrate, Ba^{++} associates with the solvent molecule in the co-sphere and stabilises the solvent structure and even it seems to predominate over the structure-breaking properties of its partner. ΔE^{*} of viscous flow remains constant with an increase in concentration of Barium nitrate, ΔS^{*} decreases and ΔF^{*}

increases slightly. It indicates that Barium nitrate is structure-maker.

Results on the study of viscosity of Calcium nitrate are included in Chapter IV. The effect of change in concentration of electrolyte, methanol concentration and temperature is similar to that of Barium nitrate. Applicability of Jones-Dole equation, Vand equation, Moulik equation and Thomas equation is discussed. Values of A coefficient are very small and even negative. It clearly indicates very weak ion-ion or solute-solute interaction. The value of A increases with temperature as well as with increase of methanol content at a particular temperature. Dependence on ionic radii the ion-ion interaction is of the order of $Ca^{++} > Ba^{++}$. 'B' coefficients are all positive but small in magnitude and decreases with increase in temperature as well as with increase in methanol concentration at a particular temperature. The value of dB/dT is negative therefore Calcium nitrate behaves as structure maker/promoter. Considering the dependence on charge density, 'B' coefficients vary in the order of $Ca(NO_3)_2$ > $Ba(NO_3)_2$. And according to ionic radii the ion-solvent interaction should be $Ba^{++} > Ca^{++}$. Vand equation and Moulik equation is valid in the concentration range 0.06 - 0.15 M for Calcium nitrate. In case of Vand equation the parameters $\bar{V}$ and θ both increases with temperature and methanol concentration. The value of $\bar{V}$ of solute in methaol solutions is seen to increase indicating that the ions get more and more hydrated in the presence of methanol. Ca^{++}

seems to be an electrostrictive structure-making ion with positive ionic volumes ($\bar{V}_{\pm}$) hydration numbers (NB) and entropy changes (ΔS^{*}). Moulik equation is not valid below 0.1 M concentration. In case of Moulik equation, the viscosity parameters `M' and `K'' of Calcium nitrate are higher than those of Barium nitrate for the sane temperature and methanol concentration. Thomas equation is not valid for Calcium nitrate in the concentration range 0.02 - 0.15 M.

The activation parameters ΔE^{*}, ΔS^{*} and ΔF^{*} of viscous flow of solutions of Calcium nitrate are more than those of solvent. It clearly indicates that there is little solute-solvent interaction Ca^{++} predominates over the structure-breaking properties of its partner. ΔE^{*} of viscous flow remains constant with an increase in cencentration of Barium nitrate, ΔS^{*} decreases and ΔF^{*} increases slightly. It indicates that Calcium nitrate is structure-maker.

From the above discussion it is clear that both the electrolytes are structre-makers/promoters. Ion-solvent interaction is more for Ba^{++} ion than that of Ca^{++} ion.