CHAPTER - V

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ELECTRICAL CONDUCTIVITY AND VISCOSITY OF SOME METAL SALTS IN AQUEOUS UREA SOLUTION

The viscosity of electrolyte solutions is a question of considerable industrial 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, urea, stand out in virtue of its high solubility in water but its 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 and conductivity of Lithium chloride in urea-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 dioxan-water methanol water, water-pyridine, water-Y-picoline, water-ter butyl alcohol mixtures at different temperatures is taken. A brief survey of earlier work of conductivity on various system is also given. A survey of measurement of conductivity of various electrolytes in Dioxan-water, dimethyl sulphoxide-water, ethylene glycol-water, o-chlorophenol and its mixtures with nitrobenzene and monobromo acetic acids and its mixture with nitrobenzene at different temperatures is taken.

Scope of the present work is also discussed in brief.

Chapter-II deals with the experimental methods adopted for 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 precaution have been given in detail. For conductivity measurement Toshniwal "Digital conductivity meter" Type CL01. 10A was used. An "imersion on dip type" conductivity cell was used with cell constant 0.87.

Results on study of viscosity of lithium chloride in urea-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 urea concentration and the effect of temperature. It is observed that viscosity (η) and relative viscosity (η_r) increase with concentration of lithium chloride. At a given temperature and for a certain concentration of lithium chloride the viscosity (η) and relative viscosity (η_r) decreases as proportion of urea increases. The applicability of Jones-Dole equation, Vand equation, Thomas equation

Moulik equation is discussed. The results show that the Jones-Dole equation is applicable for Lithium chloride in the concentration range studied i.e. from 0.1 to 2.0 M. B coefficients are all positive but small in magnitude and decrease with increase in temperature as well as with increase in urea content at a particular temperature. The value of dB/dT is negative therefore, Lithium chloride behaves as structure maker/promoter. The B coefficient becomes smaller and smaller with the increase in urea content.

Vand equation is valid in concentration range 0.4 M to 2.0 M of lithium chloride. The viscosity parameters V and Q both decrease with temperature and urea concentration, indicating Li^+ ions to be electrostrictive, structure making ions with positive ionic volume (V±), hydration number (NB) and entropy change. Moulik equation is valid for lithium chloride in concentration range 0.3 M to 0.75 M. The viscosity parameter 'M' increases with increase in temperature and decreases with concentration of urea. The constant K decreases with increase in temperature and concentration of urea. Thomas equation is found to be invalid for lithium chloride in the concentration range 0.1 M to 2.0 M.

The activation parameters ΔE^*, ΔS^* and ΔF^* of viscous flow for solutions of Lithium chloride are higher than those for solvent. It clearly indicates that there is little Solute-solvent interaction. Also it indicates structure making effect of Lithium chloride. Li^+ associates with the solvent molecules in the co-sphere and stabilises the solvent structure and even it seems to predominate over structure breaking properties of its partner. ΔE^* of viscous flow remains constant with an increase in concentration of lithium chloride, ΔS^* decreases and ΔF^* increases slightly. It indicates that Lithium chloride is structure-maker.

Results on study of conductivity of Lithium chloride are included in chapter IV. These include the determination of equivalent conductivity of solution with respect to effect of change in concentration of electrolyte, the effect of urea concentration and the effect of temperature. It is observed that equivalent conductivity decreases with increase in concentration of lithium chloride At a given temperature for a certain concentration of lithium chloride, the equivalent conductivity increases as content of urea increases. At a given concentration of urea, for a certain concentration of Lithium chloride, equivalent conductivity increases with temperature.

The results show that Debye-Huckel equation is applicable for Lithium chloride in low concentration range (0.008 M to 0.1 M). The results have been investigated for ion-pair formation also. The graph of log C and log C and $\Lambda\sqrt{C}$ vs C were studied. It has been seen that the plots are non-linear. Since for ion-pair formation there is linear relationship between log C and $\log \Lambda_c$ as well as $\Lambda\sqrt{C}$ and C. The graphs should be straight line. In case of lithium chloride the values increases and then decreases resulting the plot non-linear. It indicates that ion-pair formation is not possible.

The Walden product ($\Lambda_o\eta_o$) was also studied. It is seen from the results that as urea content is increased the walden product increases. It is further observed that walden product increases with rise of temperature. The positive temperature coefficient indicates that LiCl is structure maker or promotor.

From the above discussion it is clear that lithium chloride is structure maker/promotor, confirmed by viscosity measurements, thermodynamic properties and conductivity measurements. It has been observed that B values are decreasing with increase in urea content as well as increase in temperature. Since urea is basic and water automatically acts as an acid, the three dimensional water structure is broken down and B coefficient is expected to decrease with increase in urea content. The latter is in conformity with experimental results, so urea is structure breaker.