Chapter I

Summary of the Works Done

In this dissertation, a systematic and comprehensive study of a polyelectrolyte in mixed solvent media has been carried out from electrical conductivity, viscosity and density measurements in order to elucidate the behaviour of various types of interactions prevailing in solution.

Binary mixtures of acetonitrile and water have been chosen as the solvent system in the present study.

NaCMC, obtained from modification of a polysaccharide, cellulose, is used as the polyelectrolyte in this investigation. NaCMC is an important industrial polymer with a wide range of applications.[1-7] So the present study is expected to help extend the fruitful use of this class of polymers.

The present dissertation has been divided into nine chapters.

Chapter I (the present chapter) gives a brief account of the works done in this dissertation.

Chapter II forms the background of the present work. After presenting a brief review of the notable works in the field of polyelectrolyte solution chemistry, properties like conductance, viscosity and apparent and partial molar volumes have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion interactions were discussed with special reference to the influence of these interactions on the macroion conformations and the extent of counterion dissociation in polyelectrolyte solutions.

Chapter III describes the experimental techniques used to obtain the results presented in the dissertation.

Chapter IV reports the electrical conductivities of solutions of NaCMC in acetonitrile-water mixed solvent media containing 10, 20 and 40 volume percent of acetonitrile at 303.15, 308.15 and 313.15 K in absence of an added salt. The applicability of the Manning theory[9] for conductivity of salt-free polyelectrolyte solutions is examined and a major deviation from the theory was observed. Possible reasons for this deviation have been discussed. The effects of temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fractions of uncondensed counterions were also investigated.

Chapter IV-A describes the application of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et. al.*[10] using the scaling theory approach to the experimental results of electrical conductivity of NaCMC in acetonitrile-water mixtures. We have been able to quantitatively describe the electrical conductivity behaviour of NaCMC in acetonitrile-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

In Chapter V, the electrical conductivities of NaCMC in acetonitrile-water mixed solvent media in presence of some simple 1:1 salts (NaCl, KBr and KI) and a 1:2 salt (Na_2SO_4) have been reported at 308.15 K. Influence of the salts and their concentrations on the electrical conductivity behaviour of NaCMC is discussed. The results obtained highlighted the importance of several factors *e.g.*, the electrophoretic countercurrent, solvodynamic interactions, changing polyion conformation and the apparent charge upon the polyion etc. in these solutions.

Viscosities of NaCMC in water and in two acetonitrile-water mixtures containing 10 and 20 volume percent of acetonitrile at 308.15, 313.15 and 323.15 K using the isoionic dilution technique have been reported in Chapter VI. The influences of the medium, the temperature, and the total ionic strength on the intrinsic viscosities as well as on the Huggins constants have been interpreted from the points of view of the solvodynamic and thermodynamic interactions prevailing in the polyelectrolyte solution under investigation.

Chapter VII reports the viscosities of NaCMC in acetonitrile-water mixed solvent media both in absence and in presence of NaCl with varying concentrations. Effects of temperature and solvent composition have also been examined. The variations of the intrinsic viscosity and the

Huggins constant with temperature and solvent medium have been used to interpret the variation in the coiling of the polyion chain and counterion condensation.

Chapter VIII describes the partial molar volumes of NaCMC in acetonitrile-water media containing 10, 20 and 40 volume percent of acetonitrile at 298.15, 308.15, 313.15 and 318.15 K. This study indicates that in acetonitrile-water mixed solvent media, the counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Moreover, the polyion is found to govern the volumetric behaviour of the polyelectrolyte as a whole in these solutions. The predominance of the combined influence of the polyion-solvent electrostrictive interactions and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium was observed. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

The dissertation ends with some concluding remarks in Chapter IX.

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