Chapter I

Summary of the Works Done

In this dissertation, a systematic and comprehensive study of the solution behavior 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. Influence of this polyelectrolyte on the aggregation behavior of a surfactant in mixed solvents have also been investigated using conductometry and tensiometry.

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

NaPSS is used as the polyelectrolyte species and CTAB as the surfactant molecule in this investigation. NaPSS is an important industrial polymer with a wide range of applications, for example as a superplastifier in cement, as a dye improving agent for cotton, as proton exchange membranes in fuel cells, as a medication for treating abnormally high potassium levels.[1-4] 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 and polyelectrolyte-surfactant interactions, properties like conductance, viscosity, apparent and partial molar volumes of polyelectrolytes solutions, and conductance and surface tension in connection with polyelectrolyte-surfactant interactions have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion interactions and polyion-surfactant 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. Purifications of the chemicals used have also been discussed. (Appendix provides an account of the determination of the limiting equivalent conductivity of sodium ion in acetonitrile-water mixed solvent media.)

Chapter IV reports the electrical conductivities of solutions of NaPSS in acetonitrile-water mixed solvent media containing 20 and 40 volume percent of acetonitrile at 308.15, 313.15, and 318.15 K in absence of an added salt. The applicability of the Manning theory[5] 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. The applicability of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et. al.*[6] using the scaling theory approach to the experimental results of electrical conductivity of NaPSS in acetonitrile-water mixtures was also tested. We have been able to quantitatively describe the electrical conductivity behaviour of NaPSS in acetonitrile-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

In Chapter V, the electrical conductivities of NaPSS in acetonitrile-water mixed solvent media containing 10, 20, and 40 volume percent of acetonitrile at 308.15, 313.15, and 318.15 K in presence of sodium chloride (NaCl) have been reported. Influence of this salt on the electrical conductivity behaviour of NaPSS 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.

In Chapter VI, the intrinsic viscosities of NaPSS in water and in three acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15, and 318.15 K using the isoionic dilution technique have been obtained. 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 NaPSS in acetonitrile-water mixed solvent media both in absence and in presence of NaCl with varying concentrations. Effects of solvent composition have also been examined. The variations of the intrinsic viscosity and the Huggins constant with the 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 NaPSS in acetonitrile-water media containing 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15, 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.

Chapter IX reports the aggregation behaviour of CTAB both in absence and in presence varying concentration of NaPSS in acetonitrile-water mixed solvent media at 308.15, 313.15, and 318.15 K. NaPSS induced self-aggregation of CTAB at a concentration much lower than its *cmc* values in the mixed solvent media. The system has evidenced different kinds of interacting features corresponding to polyelectrolyte-induced aggregate formation, CTAB aggregate-NaPSS binding in bulk, CTAB-NaPSS binding at the interface, and free micelle formation in solution. The critical aggregation concentrations (*cac*), polymer saturation concentrations (*psc*), and apparent critical micellar concentrations (*cmc**) for NaPSS-CTAB interactions have been determined from tensiometry and conductometry. Good agreement between the values obtained from these two techniques was found. The results have been discussed in terms of various interactions prevailing in the present system.

The dissertation ends with some concluding remarks in Chapter X.

References

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