Chapter 1

Summary of the Works Done

The present dissertation addresses the issue of various types of interactions prevailing in solutions of a polyelectrolyte – sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media using three well-established experimental techniques.

Sodium polystyrenesulphonate is an important industrial polymer with a wide range of applications, for example it is used 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 etc.[1-4] The present study is, therefore, expected to help extend the fruitful use of this polymer.

This dissertation has been divided into ten chapters.

Chapter 1 (the present chapter) gives a brief account of the works done in this dissertation.

Chapter 2 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 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 3 describes the experimental techniques used to obtain the results presented in the dissertation.

Chapter 4 reports the electrical conductivities of solutions of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixed solvent media within the temperature range 308.15 – 313.15 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 discrepancy against this 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 5 describes the application 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 sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures. We have been able to quantitatively describe the electrical conductivity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

In Chapter 6, the electrical conductivities of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media within the temperature range 318.15 – 323.15 K in presence of sodium chloride have been reported. The conductance data have been analyzed on the basis of an equation developed in this study following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a semidilute polyion chain according to Dobrynin *et al.*[7] Excellent quantitative agreement between the experimental results and those using the equation developed was observed.

Intrinsic viscosities of sodium polystyrenesulphonate in water and in 2-ethoxyethanol-water mixed solvent media within the temperature range 308.15 – 323.15 K obtained using the isoionic dilution technique have been reported in Chapter 7. 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 operative in the polyelectrolyte solution under investigation.

Chapter 8 reports the viscosities of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media both in absence and in presence of NaCl with varying concentrations within the temperature range 308.15 – 323.15 K. 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 9 describes the apparent molar volumes of sodium polystrenesulphonate in 2-ethoxyethanol–water mixed solvent media within the temperature range 318.15 – 323.15 K. This study indicates that in 2-ethoxyethanol–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. A delicate balance of the influences of the volumetric terms, namely the void-space partial molar volume ($\overline{V}^{0}_{str}$), the electrostriction partial molar volume ($\overline{V}^{0}_{elec}$) and the caged partial molar volume ($\overline{V}^{0}_{cage}$) is found to control the volumetric behaviour of this polyelectrolyte in 2-ethoxyethanol–water mixed solvent media. 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 10.

References

1. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, Ch. Seidel and D. Stscherbina, *Polyelectrolytes Formation, Characterization and Applications*, Hanser Publisshers, Munich (1994).
2. D. H. Napper, *Polymeric Stabilization of Colloid Dispersions*, Academic Press, New York (1983).
3. E. Dickenson, *Curr. Opin. Colloid Interf. Sc.*, **3**, 633 (1998).
4. H. Yaseen, M. Khalaf, A. Dana N. Yaseen and M. Darwich, *Am. J. Perinatol.*, **25**, 3 (2008).
5. G. S. Manning, *J. Phys. Chem.*, **79**, 262 (1975).
6. R. H. Colby, D. C. Boris, W. E. Krause and J. S. Tan, *J. Polym. Sci. Part B: Polym. Phys.*, **35**, 2951 (1997).
7. A.V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).