Chapter I

Summary of the Works Done

In this dissertation, a systematic and comprehensive study of the solution behaviour of a polyelectrolyte in mixed solvent media has been carried out from electrical conductivity and viscosity measurements in order to elucidate the behaviour of various types of interactions prevailing in solution. Influence of this polyelectrolyte on the aggregation behaviour of an oppositely charged surfactant in mixed solvents has also been investigated using conductometry, tensiometry, and viscometry.

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

Sodium polystyrenesulfonate (NaPSS) is used as the polyelectrolyte and cetyltrimethylammonium bromide (CTAB) as the surfactant in this investigation. NaPSS is an important industrial polymer with a wide spectrum 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] The present study is, therefore, expected to help extend the fruitful use of this class of polymers.

The present dissertation has been divided into ten chapters.

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

Chapter II forms the background of the present work. After giving a brief review of the notable works in the field of polyelectrolyte solution chemistry and polyelectrolyte-surfactant interactions, properties like viscosity and conductance of polyelectrolyte solutions, and conductance, surface tension, and viscosity in connection with polyelectrolyte-surfactant systems have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion interactions and polyion-surfactant interactions have been discussed with special reference to the influence of these interactions on the polyion conformations and the extent of counterion dissociation in such solutions.

Chapter III describes the experimental techniques used to obtain the results presented in the dissertation. Purifications of the chemicals and the solvents used have also been discussed.

Chapter IV reports the electrical conductivities of solutions of NaPSS in methanol-water mixed solvent media containing 8, 16, 25 and 34 mass% of methanol at 308.15, 313.15, 318.15, and 323.15 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 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 methanol-water mixtures was also tested. We have been able to quantitatively describe the electrical conductivity behaviour of NaPSS in methanol-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions. The effects of temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fractions of uncondensed counterions have also been investigated.

In Chapter V, the electrical conductivities of NaPSS in methanol-water mixed solvent media containing 8 and 16 mass% of methanol at 308.15, 318.15, and 323.15 K in presence of sodium chloride (NaCl) with varying concentrations have been reported. The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter[7] following the model for the electrical conductivity of solutions of semidilute polyelectrolytes without added salt proposed by Colby *et al.*[6] using a scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[8] Excellent aggrement with the experimental results were obtained.

Chapter VI reports the viscosities of NaPSS in water and in three methanol-water mixtures containing 8, 16, and 25 mass% of methanol at 308.15 K 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 VII gives a description of an investigation on the viscosities of NaPSS in water as well as in methanol-water mixed media in presence of four low molar-mass electrolytes, namely, NaCl, KCl, NaBr and KBr having concentrations of 0.10 and 0.50 $mol.L^{-1}$. The reduced viscosities of the polyelectrolyte solutions are found to vary linearly with polymer concentration for all the systems investigated which enabled us to determine the intrinsic viscosities of sodium polystyrenesulfonate in methanol-water mixtures following the Huggins equation. An inspection of the intrinsic viscosity values reveals that the coiling of the polyion chains increases in the order: NaPSS-NaCl < NaPSS-NaBr < NaPSS-KCl < NaPSS-KBr. The solvodynamic dimensions of the polyion coil are found to be reduced as the relative permittivity of the medium decreases with the increasing amount of methanol in the mixed solvent media. This study also indicated that the polyion structures become more compact with increasing salt concentration in the medium.

Chapter VIII reports the aggregation behaviour of CTAB both in absence and in presence of varying concentration of NaPSS in methanol-water mixed solvent media at 308.15, 318.15, and 323.15 K. The polyelectrolyte induced self-aggregation of CTAB at a concentration much lower than its critical micellar concentration (*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 types of interactions prevailing in the present system.

Chapter IX reports the viscometric behaviour of NaPSS and CTAB in methanol-water mixed solvent media. The experimental results of the specific viscosity of the polyelectrolyte solutions with added surfactant have been nicely described using a simple viscosity model [9] based on the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions.[8] The present analysis indicated the formation of spherical micelles of CTAB molecules in methanol-water mixed solvent media in presence of the polyelectrolyte NaPSS.

The dissertation ends with some concluding remarks in Chapter X.

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. Sci.*, **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. R. De and B. Das, *J. Chem. Eng. Data*, **55,** 2108 (2010).

8. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).

9. N. Plucktaveesak, A. J. Konop, and R. H. Colby, *J. Phys. Chem. B*, **107**, 8166 (2003).