

Chapter X

Concluding Remarks

Polyelectrolytes show numerous interesting properties that are now being actively investigated in many laboratories. Many important information and concepts on aqueous polyelectrolyte solutions both in absence and in presence of low molar-mass electrolytes have been derived from studies on their electrical conductivity and viscosity. Moreover, electrical conductivity, viscosity, and surface tension studies on polyelectrolytes in presence of surfactants provide important information on polyelectrolyte-surfactant interactions. However, very little attention has been paid to polyelectrolyte solutions in absence as well as in presence of electrolytes and surfactants in mixed solvent media despite that fact that the study of polyelectrolytes in these media is important in the sense that such studies can offer insights into the understanding of fundamentals of polyelectrolytes. The effect of electrostatic interactions on the solution behaviour of polyelectrolytes in absence as well as in presence of an oppositely charged surfactant can be investigated conveniently by varying the composition of the mixed solvent media and this is important in understanding the characteristic behaviour of polyelectrolytes and the nature of their interactions with surfactant species. We have, therefore, investigated the behaviour of surfactant-free and surfactant-containing solutions of sodium polystyrenesulfonate in methanol-water mixed solvent media using the techniques mentioned above with a view to obtain a precise information on polyelectrolyte-surfactant interactions.

Electrical conductivities provided valuable information on the condensation of counterions onto the polyion chain in salt-free solutions. A model put forward by Colby *et al.* [*J. Polym. Sci. Part B: Polym. Phys.*, **35**, 2951 (1997)] using the scaling description proposed by Dobrynin *et al.* [*Macromolecules*, **28**, 1859 (1995)] for the configuration of a polyelectrolyte chain in semidilute solution offered a sharp improvement over the Manning counterion condensation model. Electrical conductivities of the polyelectrolyte in presence of salts underlined the importance of various factors namely, electrophoretic countercurrent, solvodynamic interactions, salt-induced conformational changes in the polyion structure and hence a concomitant change in the apparent charge of the polyion *etc.* in polyelectrolyte solutions. The intrinsic viscosities and the Huggins constants of sodium polystyrenesulfonate in methanol-water mixed solvent media were obtained in presence of an excess of an added electrolyte where neutral polymer behaviour could be recovered. Viscosity studies shed light

on the coiling/expansion of the polyion chains in solvents with varying relative permittivities. Studies on the influence of the solvent medium on the complexation of the present polyelectrolyte with a cationic surfactant, cetyltrimethylammonium bromide, and the aggregation of the surfactant molecules induced by the polyelectrolyte using conductometry and tensiometry provided important information on the polyelectrolyte-surfactant complexation and polyelectrolyte-induced aggregation behaviour. The viscometric behaviour of the present polyelectrolyte-surfactant system in methanol-water mixed solvent media have been nicely described using a simple viscosity model based on the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions. Moreover, the present analyses indicated the formation of spherical cetyltrimethylammonium bromide micelles in presence of the polyelectrolyte.

However, it is necessary to remember that interactions in solutions containing polyelectrolytes are very complex in nature because of the coupling of the macromolecular properties with the electrolyte properties of these species. Investigation in mixed solvent media provides the opportunity to study the behaviour of polyelectrolyte solutions from a more general point of view compared to those in aqueous solutions since use of a series of mixed solvents corresponds to a gradual change in the relative permittivity of the media and hence in the interactions prevailing in these solutions. More extensive studies on the different thermodynamic and transport properties of a variety of polyelectrolytes both in absence and in presence of salts and surfactants in different mixed solvent media will be of immense help in understanding the nature of various interactions in polyelectrolyte solutions. A multi-method attack to this intricate problem - like the one presented here - might be very helpful in this regard.