Chapter 10

Concluding Remarks

Polyelectrolytes exhibit numerous interesting properties that are now being actively investigated in many laboratories. Many important information and concepts on aqueous polyelectrolyte solutions have been derived from studies on their electrical conductivity, viscosity and density. However, very little attention has been paid to polyelectrolyte solutions in mixed solvent media despite the fact that the study of polyelectrolytes in these media is important in the sense that it can offer insights into the understanding of fundamentals of polyelectrolytes. The effect of electrostatic interactions on the solution behaviour of polyelectrolytes can be investigated conveniently by varying the composition of the mixed solvent media and this is important in understanding the characteristic behaviour of polyelectrolytes. We have, therefore, investigated some transport and thermodynamic properties of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixed solvent media using conducttometry, viscometry and volumetry with a view to obtain precise information on the nature of interactions prevailing in such solutions.

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 polyion chain in semidilute solution offered a sharp improvement over the classical Manning counterion condensation model. There was, however, no suitable model for the description of the electrical conductivities of polyelectrolyte solutions in presence of salts when this project was taken up. During the course of this investigation, we have been successful in developing an equation 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.* Excellent quantitative agreement between the experimental results and those using the equation developed was observed. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media.

These were also obtained in presence of an excess of an added electrolyte where neutral polymer behaviour could be recovered. Viscosity studies provided important insight into the coiling/expansion of the polyion chains in solvents with varying relative permittivities. The roles of electrostriction, solvophobicity and counterions condensation and their desolvation have been conveniently assessed from volumetric studies.

It is, however, necessary to remember that interactions in polyelectrolyte solutions are very complex in nature because of the coupling of the macromolecular properties with the electrolyte properties of these species. Investigations in mixed solvent media provide 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 occurring in these solutions. More extensive studies on the different thermodynamic and transport properties of a variety of polyelectrolytes in different mixed solvent media will be of immense help in delineating the nature of various interactions in polyeletrolyte solutions. A multi-method attack to this intricate problem of the solution behaviour of different polyelectrolytes - like the one presented here - might be very helpful in this regard.