Chapter IX

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 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 that 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 carboxymethylcellulose in acetonitrile-water mixed solvent media using the techniques mentioned above 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 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 method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium carboxymethylcellulose in acetonitrile-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 shed light on 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 the partial molar volume studies.

However, it is 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 prevailing 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 understanding 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.