Chapter 9

Concluding Remarks

Polyelectrolytes demonstrate numerous interesting properties that are now being widely investigated in many laboratories. Many significant 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 a selected polyelectrolyte sodium carboxymethylcellulose in methanol-water mixed solvent media using conductometry, 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. 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 polyelectrolytes. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium carboxymethylcellulose in methanol–water mixed solvent media. Intermolecular and intramolecular contribution has also been separated from purely experimental point of view in the said mixed solvent media.

Determination of intrinsic viscosity in absence of added salt had been very problematic for a long time because of the polyelectrolyte effect. However we have successfully obtained intrinsic viscosity for three samples of the said polyelectrolyte by using Wolf approach both in absence and presence of an added electrolyte. We have proposed a new method for the determination of the unperturbed and the perturbed root-mean-square radii of gyration of the polyion chains from the intrinsic viscosity values. This new approach may be useful in various branches of nanoscience.

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.