

Preface

Scope and Object of the Work

Polyelectrolytes are a fascinating class of polymers which have been extensively investigated for more than 7-8 decades. These still continue to be a very active area of research in a variety of fields *e.g.*, chemistry, physics, biology, medicine, materials science and nanotechnology. The widespread interest in the area of polyelectrolytes stems from the scientific curiosity in understanding their behaviour and also from their enormous potential in commercial applications. Polyelectrolytes have been utilized to assemble nanostructured materials with desired properties. Potential applications in medicine and biomedical engineering are also being vigorously pursued. Polyelectrolytes complexed with conjugated polymers such as polythiophenes and polyanilines are being used commercially as conducting coatings. These are widely used in industry as surface-active agents for water treatment and oil-spill treatment. These also find applications in the industrial production of personal care products, cosmetics, pharmaceuticals, biosensors, surfactants, absorbents, ion exchange resins, stabilizers, adhesives, paints, papers etc. A very promising and emerging area of application of polyelectrolytes is the assembly of thin films of novel materials.

Physicochemical properties of polyelectrolyte solutions have been studied for several decades, but several of them have not yet found a satisfactory theoretical explanation. In many cases a qualitative understanding is available, but a quantitative understanding is still awaited. For others, the origin of the phenomena observed remains partly obscure, indicating that the present treatment of the polyelectrolyte behaviour is incomplete and that some fundamental new views are required to gain a full understanding. Keeping in view of widening fields of applications based on the specific properties of the polyelectrolytes, it, thus, appears that the situation is far from satisfactory.

In recent years, the study of polyelectrolytes has seen a revival stimulated by the use of newly available experimental techniques and the introduction of new theoretical approaches.

Although new insight has been gained, no real breakthrough has been realized so far and much remains to be done.

The study of polyelectrolyte solutions has been conducted very extensively in aqueous solutions.¹⁻⁷ This is partly because many polyelectrolytes, usually with high charge densities, are difficult to dissolve in solvents other than water. Moreover, because of the great interest in the naturally occurring polyelectrolytes such as proteins, nucleic acids, and polysaccharides in aqueous medium, the behaviour of these species in aqueous solutions has become a main subject of study.⁷⁻¹⁰

The main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between the ionic sites in the polymer chain and secondly, the interactions between the polyions and counterions surrounding the polyion chains. The first factor is concerned with the expansibility of the polymer chains, whereas the second is not only reflected in counterion binding but also in the amount of solvation and the solvent structure in the vicinity of polyelectrolytes. Both of these factors are related to the relative permittivity of the solvent media. Use of a series of mixed solvents corresponds to a systematic change in the relative permittivity of the media and hence allows us to study the behaviour of polyelectrolyte solutions from a more general point of view.

The present dissertation, therefore, aims at elucidating the behaviour of a selected polyelectrolyte (sodium carboxymethylcellulose, NaCMC) in acetonitrile-water mixed solvent media using three different experimental techniques namely, electrical conductivity, viscosity and density.

References

1. S. A. Rice and N. Nagasawa, *Polyelectrolyte Solutions*, Academic Press, New York (1961).
2. F. Oosawa, *Polyelectrolytes*, Marcel Dekker, New York (1971).
3. E. Selegny (Ed.), *Polyelectrolytes*, D. Reidel, Dordrecht, The Netherlands (1974).
4. M. Mandel, *Polyelectrolytes*, In *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, N.M. Bikales, C.G. Overberger and G. Menges, (Eds.), 2nd ed., Wiley, New York (1988).
5. S. Förster and M. Schmidt, *Adv. Polym. Sci.*, **120**, 51 (1995).
6. H. Dautzenberg, W. Jager, J. Kötz, B. Philipp, C. Seidel and D. Stcherbina, *Polyelectrolytes: Formation, Characterization and Application*, Hanser Publishers, Munich (1994).
7. S. K. Tripathy, J. Kumar and H. Nalwa (Eds.), Vol. 2, *Handbook of Polyelectrolytes and Their Applications*, American Scientific Publishers, Stevenson Ranch (2002).
8. H. Eisenberg, *Biological Macromolecules and Polyelectrolytes in Solution*, Clarendon Press, Oxford (1976).
9. A. Veis (Ed.), *Biological Polyelectrolytes*, Marcel Dekker, New York (1970).
10. V. Bloomfield and I. L. Carpenter, *Biological Polyelectrolytes*, In *Polyelectrolytes: Science and Technology*, M. Hara (Ed.), Marcel Dekker, New York (1993).