

## Chapter 1

### Summary of the Works Done

In this dissertation, we report the results of the studies on the solution behavior of a selected polyelectrolyte in mixed solvent media. Binary mixtures of methanol and water have been chosen as the solvent system in the present study. Sodium carboxymethylcellulose (NaCMC) has been chosen as the polyelectrolyte for investigation. Sodium carboxymethylcellulose - a semi-synthetic polyelectrolyte obtained by modifying a natural polysaccharide, cellulose, - is an important polyelectrolyte with a lot of industrial and applicational aspects.<sup>1-7</sup>

The present dissertation has been divided into nine chapters.

Chapter 1 (the present chapter) gives a brief account of the works done in this dissertation.

Chapter 2 forms the background of the present work. After presenting a brief review of the notable works in the field of polyelectrolyte solution chemistry, properties like conductance, viscosity and apparent molar volumes have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion interactions were discussed with special reference to the influence of these interactions on the macroion conformations and the extent of counterion dissociation in polyelectrolyte solutions.

Chapter 3 describes the experimental techniques which have been used to obtain the results presented in the dissertation.

Chapter 4 reports the electrical conductivities of solutions of sodium carboxymethylcellulose in methanol-water mixed solvent media containing 10, 20 and 30 volume percent of methanol in absence of an added salt in the temperature range of 298.15 K – 328.15 K. The applicability of the Manning theory<sup>8</sup> for the electrical conductivity of salt-free polyelectrolyte solutions is examined and a major deviation from the theory was observed. Possible reasons for this deviation have been discussed. The effects of temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fractions of uncondensed counterions were also investigated. The applicability of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et al.*<sup>9</sup> using the scaling theory

approach to the experimental results of electrical conductivity of sodium carboxymethylcellulose in methanol-water mixtures was also tested. We have been able to quantitatively describe the electrical conductivity behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions. Variations of some of the thermodynamic parameters such as Gibbs free energy and association constants of counterion condensation on the polyion chain have been successfully determined.

In Chapter 5, the electrical conductivities of sodium carboxymethylcellulose in methanol-water mixed solvent media at 308.15 K in presence of sodium chloride, and sodium bromide have been reported. The conductance data have been analyzed on the basis of an equation developed by one of us 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.*<sup>10</sup> Excellent quantitative agreement between the experimental results and those using the equation developed was observed for both the salts.

In Chapter 6, the viscosity behaviour of sodium carboxymethylcellulose in water and in two methanol-water mixtures containing 10 and 20 volume percent of methanol at 308.15, using the isoionic dilution by using three electrolyte namely NaCl, KCl, and BaCl<sub>2</sub> has been investigated. The influences of the medium, total ionic strength, and charge on the intrinsic viscosities as well as on the Huggins constants have been interpreted from the points of view of the solvodynamic and thermodynamic interactions prevailing in the polyelectrolyte solution under investigation. Intramolecular and intermolecular contributions to the total viscosities have also been analyzed.

Chapter 7 describes the viscosities of sodium carboxymethylcellulose in aqueous and methanol-water mixed solvent media both in absence and in presence of NaCl with varying concentrations at 308.15 K. The results were analyzed in terms of a phenomenological approach for the viscosity of polymers solutions put forward by Wolf<sup>11</sup> in order to determine the intrinsic viscosities of the polyelectrolyte samples. This contribution presents a new and convenient 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 obtained in solutions with varying ionic strengths. The effect of solvent composition, molecular weight, and ionic strength on the viscosities and hence on the polyion coiling have been carefully examined.

Chapter 8 reports the apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent media within the temperature range 298.15-313.15 K. This investigation indicates that in methanol-water mixed solvent media counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Influences of the medium and the temperature on the limiting partial molar volumes have also been discussed.

The dissertation ends with some concluding remarks in Chapter 9.

## Chapter 1: Summary of the Works Done

---

### References

1. R. M. Savage, *Food Hydrocolloids*, **14**, 209 (2000).
2. E. D. Goddard, *J. Soc. Cosmet. Chem.*, **41**, 23 (1990).
3. N. N. Desai and D. O. Saha, *Polym. Prep.*, **22**, 39 (1981).
4. O. S. Zaharko, M. Przybyleki and V. T. Olivero, *Methods in Cancer Res.*, **16**, 347 (1979).
5. T. Hirato, W. Klesse and H. Ringsdorf, *Makromol. Chem.*, **180**, 125 (1979).
6. S. M. Olhero, G. Tari, M. A. Coimbra and J. M. F. Ferreira, *J. Eur. Ceram. Soc.*, **20**, 423 (2000).
7. S. K. Tripathy, J. Kumar and H. Nalwa (Eds.), Vol 3, *Handbook of Polyelectrolytes and Their Applications*, American Scientific Publishers, Stevenson Ranch (2002).
8. G. S. Manning, *J. Phys. Chem.*, **79**, 262 (1975).
9. R. H. Colby, D. C. Boris, W. E. Krause and J. S. Tan, *J. Polym. Sci. Part B, Polym. Phys.*, **35**, 2951 (1997).
10. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).
11. B. A. Wolf, *Macromol. Rapid Commun.*, **28**, 164 (2007).