

Chapter II

Introduction

Polyelectrolytes

Definition of Polyelectrolytes

The term polyelectrolyte denotes a class macromolecular compound containing a large number of ionizable or ionic groups which are soluble in a suitable polar solvent (generally water). Technically speaking, polymers which undergo ionization in solution are referred to as polyelectrolytes. Some common examples of the polyelectrolytes include proteins, nucleic acids, carrageenans, pectins, xanthan gum, polyacrylic acid and polystyrenesulfonate. Under appropriate conditions in solution, the ionizable groups of polyelectrolyte molecules dissociate into the polyions (also known as macroions) and a number of oppositely charged small ions commonly referred to as the counterions. The electrostatic interactions between the charges on the polyion chain and those between the polyion and the surrounding counterions play very important roles in determining the behaviour of polyelectrolytes in solution, which are quite distinct from that of the non-polyelectrolytes. The conformations of polyelectrolytes in dilute solutions depend on the fraction of charged groups on the polymer and the ionic strength of the solution. For weakly charged polyelectrolytes (or macromolecules carrying a small percentage of ionizable groups) the interplay between the non-Coulombic interactions such as van der Waals interaction, hydrogen bonding and other molecular interactions play an important role in governing the conformation of this kind of macromolecules. The behaviour of polyelectrolytes is also governed by such factors as the solution pH , nature of the ions, molecular weight, solvent polarity, temperature etc. Moreover the presence of the multivalent counterions significantly influences the structure and dynamics of the polyelectrolyte solutions.

Classification of Polyelectrolytes

There are different ways of classification of polyelectrolytes. It is possible to distinguish between natural, synthetic and chemically modified natural polyelectrolytes. Examples are DNA, sodium polystyrenesulfonate and carboxymethylcellulose, respectively. Polyelectrolytes may be

grouped into linear, branched and cross-linked chains or into homo and copolymers. A polyelectrolyte could be a polyacid, a polybase or a polyampholyte depending upon whether the ionizable groups are all anionic, cationic or a mixture of both. Another distinction is also possible between strong polyelectrolytes, which acquire spontaneously full charge, and weak polyelectrolytes which are only partially charged upon dissolving.

Based upon the molecular architecture, polyelectrolytes have been divided into two important categories namely linear and branched polyelectrolytes. In linear polyelectrolytes, a large number of atoms are connected together to form the backbone chain. Although in a topological sense the backbone is linear, the shape of the polymer might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.¹ Branched polyelectrolytes, on the other hand, do not have linear chains and are less investigated species compared to their linear analogues.²⁻⁷ The different known branched structures are comb-like, stars (regular and irregular), H-shaped, super H-shaped polymer and dendrimers.^{3,8-13}

Polyelectrolytes could also be distinguished depending upon their conformations. Flexible polyelectrolytes (Figure 1) bear a macroion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions. Since both of these interactions occur almost simultaneously, it is rather difficult to study these systems. Sodium polystyrenesulfonate is an example of a flexible polyelectrolyte (Figure 1b). Rigid rod-like polyelectrolytes (Figure 2), on the other hand, bear a macroion which does not undergo any conformational changes due to steric constraints on such systems. Only the intermolecular Coulombic interactions determine the solution properties of these polyelectrolytes. An example of this type of polyelectrolyte is poly (*p*-phenylene) with iodine counterions (Figure 2b). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as, DNA, RNA and the tobacco-mosaic virus.

Importance of Polyelectrolytes

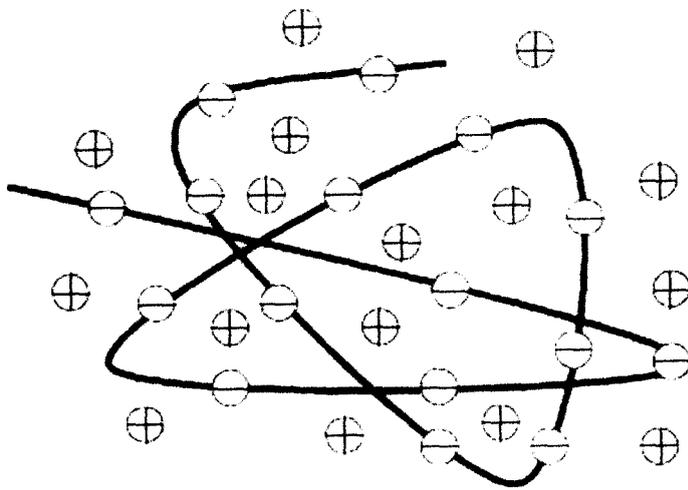
Polyelectrolytes play an important role in molecular biology and materials science. For example, the natural polyelectrolytes have been used in water-cleaning processes for centuries.

The very building block of life, the nucleic acids and proteins are polyelectrolytes. These biopolymers play a central role in maintaining and propagating life in the simplest as well as complex biological systems. Research in the area of the binding of proteins and nucleic acids, enzymes and other biological components is important to understand the mechanisms of reactions occurring in biological systems.

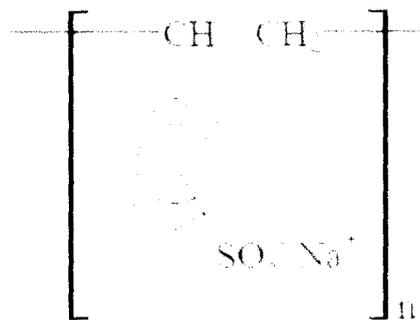
Synthetic polyelectrolytes have been a very active area of scientific research and commercial growth. Conformations of the polyelectrolytes as well as the interactions prevailing in these systems can be controlled by varying some of the parameters thus making such systems not only an interesting and rich area for exploration of novel phenomena but also an area of research which could open up new applications in variety of fields. Current applications of polyelectrolytes are in the areas of ion exchange resins, waste water treatment, oil-spill treatment, ion and gas selective membranes for fuel cells, polymeric surfactants, personal care products, cosmetics, pharmaceuticals, biosensors, absorbents, stabilizers, flocculants, etc. Potential applications in medicine and biomedical engineering are also being extensively pursued.

Concentration Regimes in Polyelectrolyte Solutions

The different properties of polyelectrolytes in solutions are very much dependent upon their concentrations in solutions. The three different concentration regimes in polyelectrolyte solutions, namely dilute, semidilute and concentrated regions, could be understood from the concept of overlap concentration which is defined as the concentration at which the polymer chains start to interact with each other *i.e.*, start to overlap. It is generally expressed as c^* . A dilute polymer solution, on the other hand, refers to the concentration region where the polymer chains are isolated and do not interact with the other chains. Here the polymer concentration is less than the overlap concentration, c^* . In dilute solutions, polyelectrolytes have a large overall size and a rather stiff local conformation.¹⁴ In the dilute regime, the chain is represented by an extended rod-like configuration of N_D electrostatic blobs of size D . Each of them, containing g_e monomers, bears a charge of $q_D = z_c f e g_e$, with z_c being the counterion valence, e the electronic charge, and f the fraction of ionized charged groups on the polyion chain (and

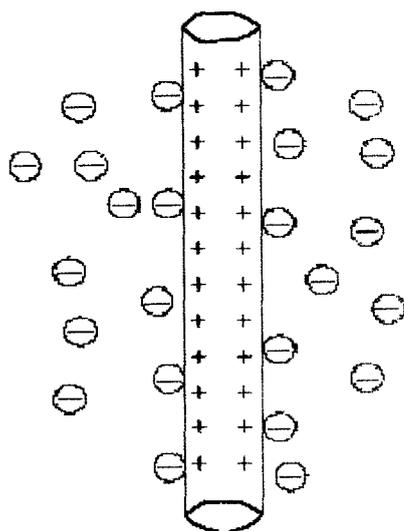


1(a)

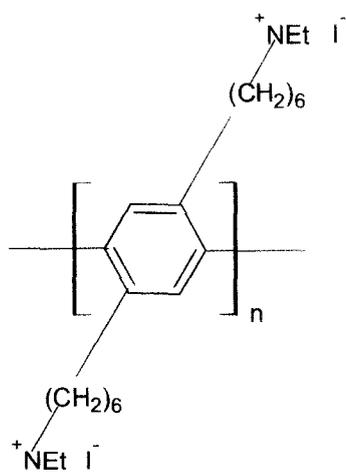


1(b)

Figure 1. (a) Schematic representation of a flexible polyelectrolyte, (b) an example: sulphonated polystyrene with sodium counterions.



2(a)



2(b)

Figure 2. (a) Schematic representation of a stiff polyelectrolyte, (b) an example: poly (*p*-phenylene) with iodine counterions

consequently, the fraction of uncondensed counterions). With increasing polyelectrolyte concentration, the chains become more flexible. When the polyelectrolyte concentration exceeds the overlap concentration c^* , the chains start to overlap and the conformations of the single chains are greatly modified. This region is commonly referred to as the semidilute regime. In semidilute solutions, the polyion chain is modelled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bears an electric charge of $q_\xi = z_c f e g$. Because of the strong electrostatic interactions within each correlation blob, the chain is fully extended conformation of electrostatic blobs in the semidilute-unentangled regime ($c^* < c < c_e$). At higher concentrations where $c > c_e$, significant overlap of neighbouring chains occurs, and this strongly affects the chain motion (semidilute-entangled regime). At even higher concentrations, the electrostatic blobs begin to overlap, and owing to the increase of electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments¹⁵ suggest a polyelectrolyte behaviour similar to that of a neutral solution. Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration c^* , at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length (*i.e.*, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the strand of N/g beads of size ξ_0). In short, a polymer solution behaves as a dilute solution for $c < c^*$, as an unentangled-semidilute solution for $c^* < c < c_e$, as an entangled-semidilute solution for $c_e < c < c_D$, and finally as a concentrated solution for $c > c_D$. Insofar as the experimental evidence is available, it confirms the existence of more concentration regimes for polyelectrolyte solutions in the absence of added low-molar-mass salt than in its presence.¹⁶ This evidence mostly stems from the study of nonequilibrium properties, such as viscosity, conductance, or diffusion. Experiments below the overlap concentration c^* are difficult to perform because of the very low concentrations and subsequently very low effects to be monitored, requiring extreme experimental sensitivity. Measurements above c_D also might be problematic, arising from the high solution viscosity. It is, therefore, not surprising that most of the experimental results described in the literature seem limited to the concentration region between c^* and c_D . The final conclusions as to the existence

of these and other possible concentration regimes require more extensive experimental investigations and further theoretical efforts.

Properties of Polyelectrolyte Solutions: A Brief Review of Important Investigations

Despite the increasing theoretical and experimental efforts over the last 7-8 decades, the solution properties of polyelectrolytes are not yet well understood. Extensive reviews and entire books have been devoted to the properties of polyelectrolyte solutions¹⁶⁻³² and no attempt is made here to provide a comprehensive review of the vast literature which exists on these subjects. In what follows, we will highlight some of the important applications of different experimental techniques to polyelectrolyte solutions with particular reference to various aspects of some the transport and thermodynamic properties of polyelectrolyte solutions as the present dissertation is concerned with such studies of polyelectrolyte solutions.

Early studies on the synthetic polyelectrolytes have been reported in the 1930s.³³⁻⁴⁰ However, the beginning of systematic studies is dated back to the mid-1940s, when a research program sponsored by the Office of Naval Research was launched at Yale, USA and Katchalsky began his studies at the Weizmann Institute, Israel.⁴¹ At the same time Kagawa in Nagoya, Japan also started an independent program on polyelectrolytes. In his first paper on polyelectrolytes, Kagawa⁴² introduced the counterion binding as an important concept in understanding the characteristic physicochemical properties of polyelectrolytes, *e.g.*, counterion activity and the dissociation constant.

Since the outset of polyelectrolyte research, electrochemical methods have been used as powerful tools to investigate and analyze the equilibrium properties as well as the transport phenomena.^{16,24,31,43} The progress in the development of sophisticated equipments and, in particular, the availability of ion selective electrodes combined with the advanced theoretical approaches, contributed to the increasing significance of conductometry and potentiometry to explore the polyion-counterion interactions. These electrochemical methods are powerful tools for providing information, which contribute to the development of the fundamental understanding of polyelectrolyte solution properties.

Solution behaviour of the polyelectrolytes can also be studied by such transport properties as viscosity, diffusion, sedimentation, and electrophoresis.^{16,19,24,25,31,43} Moreover, osmometry, dielectric spectroscopy and various scattering methods have been proven to be very useful in characterizing as well as in elucidating the behaviour of polyelectrolytes in solution.^{2,31}

The solvodynamic behaviour of polyelectrolyte molecules depends on their mass as well as on the size and shape, both modified by interaction with the third component, for example the salt, which influences the conformation of the macroion. Besides the scattering methods (discussed later), viscometry offers the possibility of studying conformational changes of polyelectrolytes, in particular, the influence of the ionic strength on the molecular dimension (please see later).

Viscosity is clearly a property of the solution as a whole under the influence of a mechanical perturbation. Diffusion phenomena, on the other hand, are directly related to the relative motion of solute particles in a stationary system. Various kinds of isothermal diffusion may be distinguished, which refer to different motions and are observed under different experimental conditions. For instance, the random motion of particles in a homogeneous system at thermodynamic equilibrium is responsible for density or concentration fluctuations. These motions are investigated by dynamic light scattering. On the other hand, diffusional fluxes arise in systems in which macroscopic chemical potential gradients exist for one or several thermodynamic species. An intermediate situation corresponds to the setup for self-diffusion measurement with fluxes of labelled molecules in a system containing a chemically identical species of different isotopic composition. All kinds of different diffusion measurements have been performed on polyelectrolyte solutions.² In the presence of macroscopic concentration gradients, diffusion of electroneutral components takes place. Diffusion is observed on the macroscopic scale where electroneutrality is observed locally. Nevertheless, with the help of special experimental techniques, the motion of the separate charged species may eventually be followed and important information regarding the effect of ion atmosphere on the macromolecular motion, changes in the average dimensions of the polyelectrolytes have already been derived.^{2,16}

In principle, sedimentation measurements should provide information about the properties of salt-free polyelectrolyte solution, but no appropriate theoretical approaches and experimental investigations are available at present, which allows the use of sedimentation measurements in this respect.⁴⁴ However, at sufficiently high amounts of supporting low molar mass electrolytes, the motion of the polyions and the counterions is largely decoupled and ultracentrifugation is a powerful tool for molecular mass determination. Additionally, the conformational changes of the polyions with the varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.^{2,45,46}

Although gel electrophoresis has been a well-established and successful tool in separation and analysis of biopolymers, especially proteins, for a long time, only a few papers were published on gel electrophoresis for synthetic polyelectrolytes.^{2,19} Information on the dependences of the polyion electrophoretic mobility on the gel concentration, electric field strength, ionic strength, chain length, charge density etc. can be obtained from electrophoresis studies.^{2,47-50}

All of the commonly measured colligative properties of simple ionic solutions *e.g.*, osmotic pressure, Donnan equilibrium etc. are also capable of characterizing polyelectrolyte solutions.² These properties have been extensively employed to a great variety of natural and synthetic polyelectrolytes to investigate the polyion-counterion interactions and the fractions of uncondensed counterions. Information on the osmotic coefficients and the Donnan equilibria of polyelectrolytes are available in the literature.^{2,16,51-56} Moreover, several investigations on the osmotic coefficients of a synthetic rod-like (rigid) polyelectrolyte solutions have also been performed to test the various models describing the electrostatic interactions of the counterions with the polyion^{55,56} and the results indicated failure of the Manning and the Poisson-Boltzmann cell models. Later, Deserno *et. al.*⁵⁷ performed an analysis of the osmotic coefficients of two rod-like polyelectrolytes namely, DNA and poly(*p*-phenylene) using molecular dynamics (MD) simulations and the Debye-Hückel-Hole-Cavity (DHHC) theory and demonstrated that they

indeed give a good description of the influence of the correlations of the counterions with the macroion.

The dielectric properties of aqueous polyelectrolyte solutions present a very complex phenomenology, not yet understood completely. Although the dielectric methods have been established for well over a century, it is still one of the most important techniques for studies of the structure and dynamics of polymer solutions. This is because it can investigate the relaxation processes occurring in aqueous polymer solutions in an extremely wide range of characteristic times, approximately from 10^{-12} through 10^3 s. Dielectric spectroscopic studies on polyelectrolyte solutions provide information about the effective charge on the polyelectrolyte chains, the fraction of condensed counterions, and the effective friction coefficient of condensed counterions. A recent review gives important information in this regard.³¹

Classical scattering methods, such as static light scattering (SLS), small-angle X-ray scattering (SAXS), and small angle neutron scattering (SANS) are of special importance in the characterization of the molecular parameters of polyelectrolytes in solution.^{32,58-61} For the past four decades there has been an increasing interest in dynamic scattering methods, particularly dynamic light scattering (DLS), because these could provide important insight into the dynamics of polyelectrolyte solutions to very high concentration, and these are also capable of providing useful structural informations, *e.g.*, translational diffusion coefficient and solvodynamic radius of the scattering species.

In particular, the main interest of light scattering studies on polyelectrolyte solutions was focused up to about 1980 on the investigation of coil expansion and the second virial coefficient in relation to the ionic strength of the medium, besides their function as routine method in determining the mass average molecular mass.⁶²⁻⁶⁶ One of the most interesting topics of static scattering experiments at present is the investigation of the interparticle arrangement of the polyelectrolyte molecules in salt-free solutions or at very low ionic strength. Compared to the light scattering experiments, small-angle X-ray scattering studies lead to structural information about small distances (2-100 nm). The main field is the investigation of the structural details of chain conformation.^{64,67,68} A further important field of application of SAXS is the



characterization of biopolymers such as proteins and nucleic acids. Besides the determination of molecular mass, information on the dimension, geometric form, and internal structure of the biopolymers is available from SAXS studies.⁶⁹⁻⁷² For unfolded proteins, the chain statistics may be checked by SAXS in combination with, for instance, static and dynamic light scattering, which provides the opportunity to determine several independent parameters such as molecular mass, radius of gyration, hydrodynamic radius, persistence length, and virial coefficient.^{73,74}

Conventional SANS experiments provide information about the mass and the radius of gyration of the aggregated clusters; the labelling technique allows the single chain conformation of the polyelectrolyte molecules incorporated into the clusters to be determined.⁷⁵⁻⁸²

Despite the variety of conformational effects that may be studied by DLS in salt-containing polyelectrolyte solutions, large number of studies have been devoted to fundamental problems of the structures of polyelectrolyte solutions at low ionic strength, and their dependence on polymer concentration, ionic strength, and molecular mass.^{2,83-85}

It can be stated that the experimental data obtained from different scattering methods as to the intermolecular structure factor of semidilute salt-free polyelectrolyte solutions are qualitatively in good agreement, but quantitative discrepancies occur and the real structure models are not clear at present. Comprehensive and sophisticated experiments are necessary to prove the theoretical models in more details. A brief and very useful review on the application of these different scattering techniques is available in Dautzenberg *et. al.*²

Although considerable attention has so far been paid to the studies of polyelectrolyte solutions using various available experimental techniques described above, there is very little work in the literature dealing with the effect of the medium in mixed solvent systems, and the temperature on the interactions between a polyion and its counterions⁸⁶⁻⁹³ despite the fact that the use of a series of mixed solvents permits alteration of the relative permittivity of the media in a systematic manner thus enabling one to study the varying polyelectrolyte behaviour in general. Studies in such systems, hence, could provide important information on the interactions between the polyions and the counterions and also on the conformation of the polyions in solution.

Here, we shall particularly dwell upon different aspects of transport and thermodynamic properties of polyelectrolytes, as the present dissertation is intimately related to the studies of electrical conductances, viscosities, and partial molar volumes of sodium carboxymethylcellulose (NaCMC), a substituted polysugar with a less flexible polymer chain, in acetonitrile-water mixed solvent media. The effects of added salt have also been investigated.

Some Important Properties of Polyelectrolyte Solutions

Polyelectrolyte Conductance

Manning Model for the Conductance of Salt-Free Polyelectrolyte Solutions^{19,94-98}

The specific conductance and the equivalent conductivity, Λ , are experimentally determined parameters which are suitable to describe the electrolytic transport properties of polyelectrolyte solutions because these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field. The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory^{19,94-98} for dilute solutions based on the counterion condensation for an infinitely long and thin line charged chain. The basic idea is that if the charge density of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy $k_B T$.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by^{19,96,98}

$$\xi = \frac{e^2}{bDk_B T} \quad (1)$$

where e is the protonic charge, D the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzmann constant

and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense on to the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law of electrical conductivity for a salt free polyelectrolyte solution is related to ξ by the following equation^{95,96}

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (2)$$

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is the polyion-counterion interaction parameter given by^{19,96,98}

$$f = \frac{0.866}{\xi} \quad (3)$$

In contrast to Huizenga⁹⁹ where the counterions are regarded either as “bound” or as “free” implying that they are not influenced by the polyion, Manning assumed that while the condensed counterions, certainly qualify as bound, the fraction of such ions is $1 - \xi^{-1} \neq 1 - f$, the uncondensed counterions may, in no way, be thought of as free, being subjected to the Debye-Hückel potential of the polyions. Thus f does not have the significance of the fraction of free counterions rather it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolyte,⁹⁷ and it follows for counterions with a charge of z_c

$$\lambda_p = \frac{279A|z_c|^{-1}|\ln \kappa a|}{1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|} \quad (4)$$

where the parameter a is the radius of the polymer chain, while

$$A = \frac{Dk_B T}{3\pi\eta_0 e} \quad (5)$$

with η_0 being the coefficient of viscosity of the solvent. In Eq. (4), κ is the Debye screening constant, which is defined by

$$\kappa^2 = \frac{4\pi e^2}{Dk_B T} \xi^{-1} n_c |z_c| \quad (6)$$

where n_c is the stoichiometric equivalent polyion concentration (monovalent charged groups per unit volume).

Limitation of the Manning Model

Since the Manning theory applies, as stated above, to highly diluted systems where the polyion-polyion interactions are assumed to be absent and to polyions modeled as a linear array of point charges, its validity is limited to very low concentration regimes of polyelectrolyte solutions.

A survey of the literature indicated that although in a limited concentration range, the change of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not generally agree with the predictions. This aspect has been amply described in the reviews by Bordi *et. al.*³¹ and Wandrey and Hunkeler⁴³ and no attempt is, therefore, made here to provide a comprehensive review of the vast literature that exists on this subject. However, some of the important results are given here. The article in which Manning presented⁹⁶ the complete theoretical equation for the equivalent conductance of a salt-free polyelectrolyte solution in the limit of zero concentration was published in 1975. Interestingly, the two subsequent articles by Kwak and Hayes¹⁰⁰ and Szymczak *et. al.*¹⁰¹ in that issue of the journal pointed out the discrepancies of this theory to describe satisfactorily the observed conductivity behaviour at finite concentrations. Kwak and Hayes¹⁰⁰ studied the electrical conductances of lithium, sodium, potassium, cesium,

magnesium, calcium, and strontium salts of polystyrenesulfonic acid covering the dilute and semidilute regimes (*i.e.*, above and below the overlap concentration, c^*) at 298.15 K. They observed a minimum in the equivalent conductivity in the range 7×10^{-3} to 1×10^{-2} monomol.l⁻¹ for all counterions and the two investigated polyelectrolytes of molar masses of 70,000 and 500,000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the increase after the minimum was passed could not be explained. It was concluded that the applicability of the Manning theory is questionable for a concentration range where chain coiling is probable. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonate in semidilute solutions were carried out by Szymczak *et. al.* at 298.15 K.¹⁰¹ Positive deviations from the limiting law are evident even at the lowest concentrations employed. They concluded that the Manning theory for electrical transport properties might require additional theoretical considerations.

Other studies of Kwak *et. al.*^{102,103} dealt with alkali metal salts of a number of ionic polysaccharides (carboxymethylcellulose, polypectate, dextran sulfate). These authors concluded from the comparison of the various polyions carrying different charge density parameters that, although qualitative agreement is obtained with the Manning limiting law, the concentration dependence predicted is in agreement with the experimental curves only for the polyions with a relatively low charge density. The behaviour of dextran sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rodlike structure on which the theory is based.

Significant deviations of the experimental equivalent conductivities of sodium and potassium dextran sulfate from the Manning predictions in the semidilute concentration regime were also reported by Beyer and Nordmeier.¹⁰⁴

The concentration dependence of the conductivity data of tetra-*n*-alkylammonium salts of pectic acid in aqueous solutions above and below the overlap concentration also manifested large deviation from the Manning limiting law.⁹²

Wandrey *et. al.*¹⁰⁵ made extensive use of the Manning model for conductivity of dilute and semidilute polyelectrolyte solutions in inert atmospheres and noted deviations from the model predictions.

Bordi *et. al.*⁹³ compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4,000, 167,000 for both the dilute and semidilute regimes. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polymer molecular weight. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molecular weight sample is hardly surprising, since these data are all above c^* , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molecular weight sample is noteworthy since these data are all below c^* .

In a study on the electrical conductivity of lithium, sodium and potassium salts of poly [(maleic acid)-*co*-(vinyl pyrrolidone)], Rios¹⁰⁶ confined the attention below the overlap concentration. Whereas the Manning model predicts a slow but monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration, a maximum was observed experimentally in each of these three cases. Although, the agreement between the experiment and theory is generally poor, theoretical curves approach the experimental ones for the lithium and sodium salts over a very narrow concentration range for very dilute solutions.

It is thus apparent that the Manning limiting law for the polyelectrolyte conductivity is inappropriate because of the various unrealistic assumptions of this theory.

Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions¹⁰⁷

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*¹⁰⁷ using the scaling description proposed by Dobrynin *et. al.*¹⁰⁸ for the configuration of a polyelectrolyte chain.

In the semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bears an electric charge of $q_\xi = zefg$ (z being the counterion valence and e is the electronic charge) and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge of $Q_p = N_\xi q_\xi = zefgN_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e . This means that for length scales less than ξ_0 , the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0 , the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Within this model, in absence of added salt, the equivalent conductivity of a polyion in a semidilute solution is given by

$$\lambda_p = \frac{Fzefg \ln(g/g_e)}{3\pi\eta_0\xi_0} \quad (7)$$

where F is the Faraday number and η_0 is the coefficient of viscosity of solvent.

Under the condition of $g/g_e = \xi_0/\xi_e$ and making use of the fact that the electrostatic blobs are space filling ($g = c\xi_0^3$, c being the number density of monomers) Eq. (4) reduces to

$$\lambda_p = \frac{Fzefc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi\eta_0} \quad (8)$$

The equivalent conductance of the polyelectrolyte solution is then given by

$$\Lambda = \frac{1}{A} \left[\lambda_c^0 + \frac{Fzefc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi\eta_0} \right] \quad (9)$$

The above expression given by Colby *et al.*¹⁰⁷ is derived taking into account the scaling arguments proposed by Dobrynin *et al.*¹⁰⁸ neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. As can be seen the above model has a single free parameter A , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge-density parameter $\xi = \lambda_B / b$, Eq. (9) can be applied to more concentrated systems, up to the concentration c_D , where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This new model has been applied, so far, to a limited number of aqueous polyelectrolytes^{31,93,107} and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify the concentration regimes differing in the fractions of uncondensed counterions.¹⁰⁹ This model, however, has not been applied to polyelectrolyte solutions in solvents besides water with the exception of an attempt by one of us for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media.¹¹⁰

Effect of Salts on the Conductance of Polyelectrolyte Solutions

Addition of salts to a polyelectrolyte solution might change its conductivity behaviour dramatically and hence studies on the conductivity of polyelectrolytes in presence of a low-molar-mass salt might provide important information on the interactions of polyelectrolytes with added salts, conformations of the polyion chains etc.

An approach which is usually used in the literature in describing the behaviour of salt-containing polyelectrolyte solutions is to analyse the experimental data phenomenologically in terms of an additivity contributions of the polyelectrolyte and the simple salt to the total specific conductivity.¹¹¹⁻¹¹⁴ Traditionally, this approach takes the form of an assumed additivity of the

specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution,

$$\kappa = \kappa_p + \kappa_s \quad (10)$$

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_s is the specific conductance of the simple salt in the absence of polyelectrolyte. In a polyelectrolyte-salt solution, therefore, the polyelectrolyte specific conductance is given by,

$$\kappa_p = \kappa - \kappa_s \quad (11)$$

If a true additivity holds, the values of κ_p obtained for a given polyelectrolyte in salt-free (where $\kappa_s = 0$) and salt-containing solutions would be identical. However, this is not observed for different polyelectrolyte-salt combinations investigated earlier.¹¹¹⁻¹¹⁴ Thus the true value of the polyelectrolyte specific conductance cannot be calculated from conductance data obtained in salt-containing polyelectrolyte solutions by using additivity of polyelectrolyte and simple salt specific conductances indicating clearly the existence polyelectrolyte-salt interactions. The observed deviation may be attributed to the changed conformation of the polyion in presence of an added salt as a result of the interactions of salt with the polyelectrolyte compared to that present in the salt-free solutions. Changes in the specific conductance contribution of the counterions in presence of a salt may also contribute to the observed deviation.

Kowblansky and Ander,¹¹¹ therefore, modified the 'primitive' additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa_p = \kappa - \kappa_s(D_2 / D_2^0) \quad (12)$$

where D_2 and D_2^0 are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of

self-diffusion coefficients D_2/D_2^0 has been used as a quantitative measure of the effective interactions of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s(D_2/D_2^0)$.

Now, in absence of the experimental data for D_2/D_2^0 for the present system, these were calculated by using the Manning theory as,¹¹¹

$$D_2/D_2^0 = 1 - (1/3)\xi X \left[2 + X(1 + \pi\xi^{-1}) \right]^{-1} \quad (13)$$

when $\xi < 1$, but when $\xi > 1$, D_2/D_2^0 takes the following form,

$$D_2/D_2^0 = 1 - (1/3)\xi^{-1} X \left[\xi^{-1} X(1 + \pi) + 2 \right]^{-1} \quad (14)$$

Here X is the ratio of the equivalent polyelectrolyte concentration (c_p) to the equivalent salt concentration (c_s), and ξ is the charge density parameter of the polyelectrolyte.

Although the modified additivity has been shown to offer some improvement over the primitive one, significant departures are also noticed in some cases.¹¹¹⁻¹¹⁴ Therefore, the effect of salts on the conductance is not described by the additivity even if the interactions among all species of ions in solution are taken into account through Eqs. (12) – (14).

These observations indicate that the effective specific conductance of the added simple salt may not be given by $\kappa_s(D_2/D_2^0)$. The derivation of the salt diffusion ratio only takes into account the relaxation effect. The effect of electrophoretic countercurrent, which is neglected while deriving Eqs. (13) and (14), might play an important role. Another possible reason might be the modification of the polyion specific conductance possibly due to its changing conformation by the addition of the salts. Overall conformation of the polyion might then be largely different from an infinitely long cylinder in the changing ionic environment. A further possibility is that the contribution of the polyion to the specific conductance may be influenced

by the solute-solvent solvodynamic interactions. Namely, the specific conductance depends on whether the polyion is free-draining or non-draining. It should be pointed out that the polyion mobility, however, has been understood not to be so sensitive to the ionic strength⁶⁷. In addition, there is no direct evidence that the conformational change provides a drastic deviation from the additivity of conductance. Further studies on different polyelectrolyte-salt systems in various solvent media might then be helpful in providing light on the interactions prevailing in such systems.

Polyelectrolyte Viscosity

Viscosity of Polyelectrolytes as a function of Concentration

Viscosity is an important tool for the determination of molecular structure and conformation of a polymer of either type neutral or charged. In case of neutral polymer solutions, the reduced viscosity η_{sp}/c_p (defined as $\eta_{sp}/c_p = (\eta - \eta_0)/\eta_0 c_p$, where η is the viscosity of the solution, η_0 is the viscosity of the solvent in the absence of polymer and c_p is the (monomer) concentration of the polymer solution) is proportional to c_p . This well-known relation is used for determining the intrinsic viscosity $[\eta]$ simply by extrapolation of η_{sp}/c_p values to $c_p = 0$. On the other hand, salt-free polyelectrolyte solutions exhibit an anomalous concentration dependence of viscosity. Early investigations of the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that reduced viscosity would increase without bound as one lowers the polyion concentration. In these studies, which are summarized in the pioneering work of Fuoss,^{115,116} a straight line is obtained when the reduced viscosity is plotted as a function of the square root of the polymer concentration. It is usually assumed that this line could be extrapolated to zero concentration and that the intercept at zero concentration gives the intrinsic viscosity. However, careful investigation of the dilute solution behaviour revealed that the apparently unbounded increase of the reduced viscosity is always followed by a maximum,¹¹⁷⁻¹²⁰ and normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. It has been argued that the observed behaviour is a consequence of screening of long-range intermolecular interactions by the residual electrolyte in the solution, an explanation supported by the observation of "regular" neutral polymer behaviour upon isoionic dilution of

polyelectrolyte solutions.¹²⁰ The anomalous shape of the curve of the reduced viscosity versus concentration for dilute salt-free solutions, found in many studies during the last four and a half decades, was generally interpreted as the result of expansion and shrinking of the flexible macroion due to short-range interactions. Most of these investigations were performed on weak polyelectrolyte systems *e.g.*, derivatives of polyvinylpyridine and polymers containing carboxylic acids, as reviewed by Tanford.¹²¹ Hodgson and Amis^{122,123} published a number of articles describing the behaviour of poly 2-vinylpyridine in ethylene glycol and interpreted the data in terms of changes in coil dimensions caused by the influence of the electrostatic persistence length as screened by counterions and excess salt ions. Because of the potential to provide information of the conformation of the polyion chains, viscosities of various kinds of aqueous polyelectrolyte solutions have been investigated. Some examples include hyaluronan and its sodium salt^{124,125} poly (galacturonic acid) sodium salt¹²⁶ sodium polystyrenesulfonate,^{118,127} NaCMC¹²⁸ polysulfobetaines,¹²⁹⁻¹³² polyelectrolytes with poly(*p*-phenylene) backbone¹³³ etc.

In 1987 Witten and Pincus put forward a theory for the viscosity of polyelectrolyte solutions which was derived for concentrations near the overlap concentration.¹³⁴ Later Cohen *et. al.*^{118,119} derived a similar relation on the basis of the theory by Hess and Klein¹³⁵ and have shown that the relation derived fits well the experimental results with some adjustable parameters. Both of these approaches are characterized by assumptions that viscosity is dominated by intermolecular interactions which are primarily electrostatic in nature and by the treatment of the solution as a simple viscoelastic liquid. However, in spite of the success of these treatments to a limited number of systems, the assumptions underlying these approaches are questionable.

Another interesting approach to the viscosity problem has been presented by Nishida *et. al.*¹³⁶ who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.¹³⁷ The interaction between the particles is described by a Debye-Hückel potential which exhibits a maximum as a function of polyion concentration. The maximum in the interaction energy is manifested by the maximum of the viscosity. The calculation may be employed to separate formally the influence of interaction and of conformational change of the polyion on experimental viscosity data.

In their approach Nishida *et. al.*¹³⁶ pointed out that in the limit of weaker interactions the influence of polymer conformation and the influence of electrostatic interactions on the intrinsic viscosity of linear polyelectrolytes may be simply additive. A similar approach is also commonly used for the description the rheology of colloidal dispersions where the influences of near-field hydrodynamics, interparticle forces and Brownian motion on the viscosity is taken as additive.

Antonietti *et. al.*¹³⁸ demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.¹³⁵ On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following equation,

$$\eta_{sp} / c_p \sim c_p / \kappa^3 \quad (15)$$

where c_p , the polyelectrolyte concentration is expressed in equiv.l⁻¹ and κ is the inverse Debye screening length.

Now, since $\kappa^2 = 4\pi l_B (c_p + c_s)$ or $\kappa^2 = 4\pi l_B (c_p / \lambda + 2c_s)$ when the charge parameter (λ) is >1 or ≤ 1 , respectively, we can write

$$\eta_{sp} / c_p \sim c_p / (c_p / \lambda + 2c_s)^{3/2} \quad (16)$$

$$\text{or } c_p / (c_p + 2c_s)^{3/2} \quad (17)$$

when λ is >1 or ≤ 1 , respectively.

Antonietti *et. al.*¹³⁹ expressed the reduced viscosity for charged latex particle as,

$$\frac{\eta_{sp}}{c_p} = [\eta] \left[1 + k' [\eta] c_p + \left(\frac{\eta_{sp}}{c_p} \right)_{HK} \right] \quad (18)$$

in which $(\eta_{sp}/c_p)_{HK}$ represents the electrostatic contribution expressed in Eq. (15). Besides describing the polyelectrolyte concentration dependence of the reduced viscosity, Eq. (18), in principle, is capable of recovering the intrinsic viscosity of the polyelectrolyte solution. In order to obtain the intrinsic viscosity using this equation, however, one needs to perform the viscosity measurements in very dilute solutions because of the nonlinear variations of the reduced viscosity with concentration.

Intrinsic Viscosity

It is well known that the intrinsic viscosity $[\eta]$ is the parameter which enables characterization of the dimension and configuration of a polymer in solution. For salt-free and low salt-containing polyelectrolyte solutions, however, the determination of this parameter presents a great challenge due to the anomalous concentration dependence of viscosity of polyelectrolyte solutions in these cases.

Determination of Intrinsic Viscosity of a Polyelectrolyte in Presence of a Large Excess of an Electrolyte

At a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity (η_{sp}/c_p) varies linearly with the polymer concentration (c_p) similar to that for a neutral macromolecular solution, provided there is an excess of low molar mass electrolyte thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation^{2,140}

$$\eta_{sp}/c_p = [\eta] + k_H [\eta]^2 c_p \quad (19)$$

here k_H is the Huggins constant which is a characteristic for a given polymer-solvent system.

Determination of Intrinsic Viscosity of a Polyelectrolyte by Isoionic Dilution

The determination of the intrinsic viscosity is more straightforward if the isoionic dilution method^{120,141} is applied. Following this method, a polyelectrolyte solution in the pure solvent (in absence of any low molar mass salt) is diluted with solutions of increasing concentration of a salt. The dilution of the solution is performed in such a way that after each addition, the total ionic strength of the solution remains the same and equal to the original value due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these conditions the reduced viscosity decreases linearly as one lowers the polyelectrolyte concentration and thus extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength. Moreover, since the ionic environment around the polyions remains unaffected as a result of isoionic dilution, the original conformation of the polyion under salt-free situation is assumed to be preserved.

In spite of the success of this method for the determination of intrinsic viscosity in a convenient manner, however, very little attention was paid to this direction so far.^{120,125,141,142}

Partial Molar Volumes of Polyelectrolytes

The partial molar volume (Φ_v) of a polyelectrolyte in solution can be calculated using the conventional equation

$$\Phi_v = \frac{M}{\rho} + 1000 \frac{(\rho - \rho_0)}{m\rho\rho_0} \quad (20)$$

where m is the polyelectrolyte concentration (in moles of monomer per kg of solvent), M the molecular mass of the monomeric unit of the polyelectrolyte under study, ρ the density of the solution and ρ_0 the density of the solvent.

In majority of the polyelectrolyte solutions investigated, the partial molar volumes were found to remain practically constant over the concentration ranges investigated though it is true that they vary slightly with concentration for a few cases.¹⁴³⁻¹⁴⁸ In the former cases, the partial molar volumes at infinite dilutions (Φ_v^0) have usually been considered as the mean of the

observed Φ_v values, whereas in the later cases these were determined by extrapolating Φ_v values to zero concentration of the polyelectrolyte. The insensitivity of the Φ_v values towards concentration was interpreted as the result of a delicate balance of two counteracting effects namely the electrostriction effect and the so-called “structure-making” effect due to the filling of intermolecular cavities of the solvent structure both of which cause a negative concentration dependence of Φ_v values and the “void space” effect (the destruction of solvent structure in the region of the ionic cosphere) which causes a positive concentration dependence of Φ_v values.^{149,150}

Various concepts concerning the electrostrictional hydration effect, the hydrophobic structural effect, and counterion-binding on to the polyion chain in polyelectrolyte solutions were interpreted on the basis of this property.^{143-146,151-153} Empirical procedures have been developed to calculate and predict the partial molar volumes for non-ionic and ionic organic compounds in aqueous solutions.^{154,155} However, the evaluation of the partial molar volumes by these procedures is limited because of the lack of availability of reliable experimental data for a broad variety of polyelectrolyte species.¹⁴⁷

Partial molar volume is an important thermodynamic property which may be helpful in elucidating the solute-solvent as well as solute-solute interactions. Moreover, this is also necessary for the application of characterization methods and physicochemical techniques including preparative and analytical ultracentrifugation, as well as SAXS and SANS.

Present Investigation

From the above discussion, it is apparent that the problem of intrapolyion and polyion-counterion interactions is intriguing as well as interesting. It is desirable to attack this problem using different experimental techniques. Moreover, 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. We have, therefore, utilized three important methods

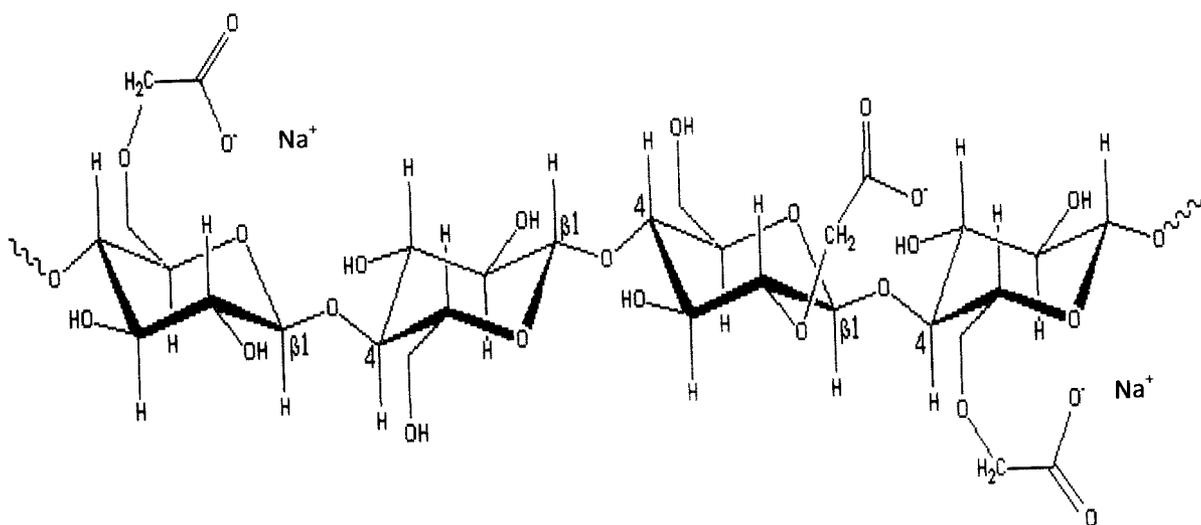


Figure 3. Structure of NaCMC

viz., conductometry, viscometry, and volumetry to study the behaviour of NaCMC in acetonitrile-water mixed solvent media.

NaCMC is a chemically modified cellulose derivative (Figure 3) with large water solubility, broadly used due to its low cost, lack of toxicity, and biodegradability. Food industry, cosmetics, pharmaceuticals, suspension agents, formulation agents in controlled release of drugs and pesticides, papers and paper products, adhesives, and ceramics provide a brief list of the numerous applications where carboxymethylcellulose is used in the acid or in the sodium salt form.¹⁵⁶

As pointed out earlier, the main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between 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 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 the systematic change in the relative permittivity of the media. In this study, the mixed solvent acetonitrile-water has been used. Acetonitrile-water solutions are among the most extensively studied of all solvent mixtures.¹⁵⁷⁻¹⁶⁴ These mixed solvents are of interest because although the two solvents are fully miscible at room temperature, the components have very different chemical natures. The relative permittivities of the mixed solvent media could be varied over a wide range. In addition, acetonitrile-water mixtures are of considerable technological interest, *e.g.*, for the recovery of precious metals from concentrates^{165,166} and for the removal of iron from hydrometallurgical leach liquors.¹⁶⁷ Extensive thermodynamic and other physical measurements have been made on acetonitrile-water mixed solvent media both in the presence and absence of dissolved electrolyte.^{157-164,168} It would be, therefore, interesting to investigate the behaviour of a polyelectrolyte in these mixed solvents.

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