

## Chapter 2

### Introduction

#### 2.1 Definition of Polyelectrolytes

In contrast to neutral polymer solutions, polyelectrolytes are one of the least understood states of condensed matters. *Electrolytes* are defined as a chemical compound composed of ions, in solid, liquid or in dissolved state. Such a system exhibits electrolytic conductivity and interionic interaction. *Polymer* is defined as a molecule of high molecular weight formed by combination of a number of small molecules (monomers).

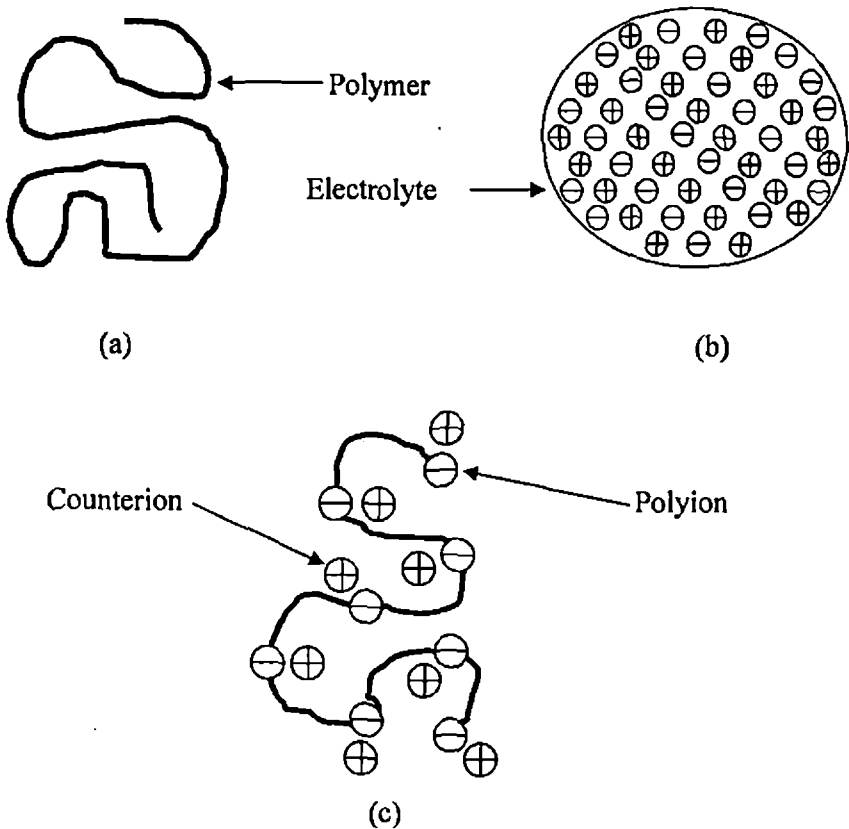


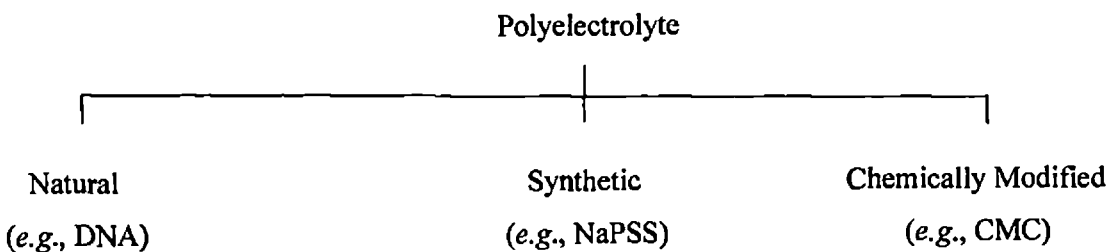
Figure 2.1 (a) Polymer, (b) Electrolyte, and (c) Polyelectrolyte

The term polyelectrolyte denotes a class of macromolecular compounds containing a large number of ionizable groups which are soluble in an appropriate polar solvent and thereby produce macroions (or polyions) along with large number of oppositely charged counterions. Some common examples of polyelectrolytes include proteins, nucleic acids, carrageenans, pectins, xanthan gum (a thickening agent produced by a bacterium that lives on cabbage plants), polyacrylic acid and polystyrenesulphonate.

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 polyions 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 their conformations. The behaviour of polyelectrolytes is also influenced by such factors as the solution  $pH$ , nature of the ions, molecular weight, solvent polarity, dielectric constant, temperature etc. Moreover the presence of multivalent counterions significantly influences the structure and dynamics of polyelectrolyte solutions.

## 2.2 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 deoxyribonucleic acid (DNA), sodium polystyrenesulphonate (NaPSS) and carboxymethylcellulose (CMC), respectively.



Polyelectrolytes may also be classified into homo- and copolymers. A polyelectrolyte could be a polyacid (*e.g.*, polystyrenesulphonic acid), a polybase (*e.g.*, polyvinylamine hydrobromide) or a polyampholyte (*e.g.*, protein) depending upon whether the ionizable

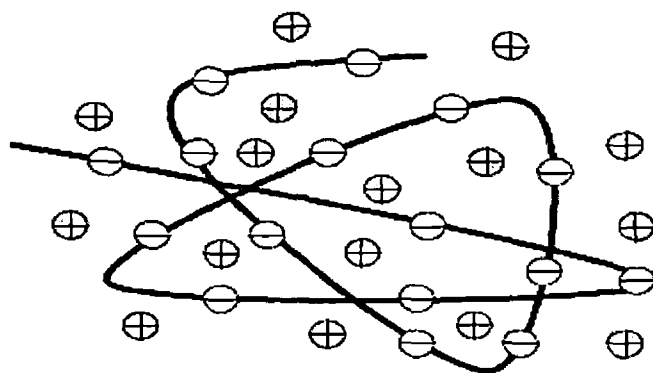
groups are all anionic, cationic or a mixture of both. Another distinction is also possible between strong polyelectrolytes (e.g., sodium polystyrenesulphonate), which acquire spontaneously full charge, and weak polyelectrolytes (e.g., polyacrylic acid) which are only partially charged upon dissolving.

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.<sup>1</sup> Branched polyelectrolytes, on the other hand, do not have linear chains and are less investigated species compared to their linear analogues.<sup>2-7</sup> The different known branched structures are comb-like, stars (regular and irregular), H-shaped, super H-shaped polymer and dendrimers.<sup>3,8-13</sup>

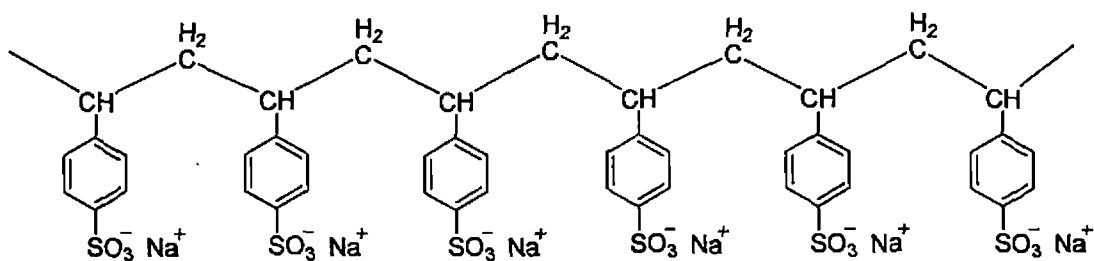
Polyelectrolytes could also be distinguished depending upon their conformations. Flexible polyelectrolytes (Figure 2.2a) bear a macroion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions. Since both of these interactions occur almost simultaneously, it is rather difficult to study these systems. Sodium polystyrenesulphonate is an example of a flexible polyelectrolyte (Figure 2.2b). Rigid rod-like polyelectrolytes (Figure 2.3a), on the other hand, bear a macroion which does not undergo any conformational change 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 2.3b). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as, DNA, ribonucleic acid (RNA) and the tobacco-mosaic virus.

### 2.3 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 blocks 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.

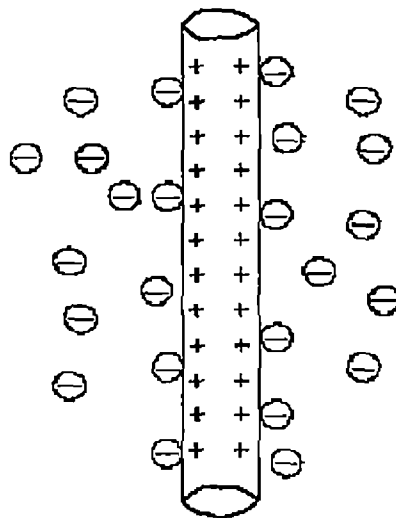


(a)

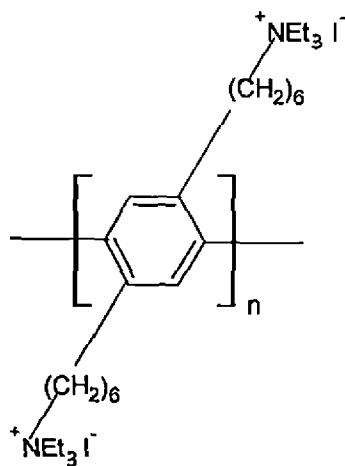


(b)

**Figure 2.2** (a) Schematic representation of a flexible polyelectrolyte and (b) an example: sulfonated polystyrene with sodium counterions.



(a)



(b)

**Figure 2.3** (a) Schematic representation of a stiff polyelectrolyte and (b) an example: poly (*p*-phenylene) with iodine counterions

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 one or more 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 possibilities of applications in variety of fields. Water soluble polyelectrolytes have found application in biochemical and medical research and deveopment. There is presently much research in using biocompatible polyelectrolytes for implant coatings, for controlled drug release, and other applications. Current applications of polyelectrolytes are also 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, soaps, shampoos, pharmaceuticals, biosensors, absorbents, etc. Potential applications in medicine and biomedical engineering are also being extensively pursued.

Polyelectrolytes have also found applications in modifying flow and stability properties of aqueous solutions and gels. For instance, they are used to initiate flocculation (precipitation) or to stabilize colloidal suspensions. To impart a surface charge to neutral particles, polyelectrolytes can also be used to enable the particles to be dispersed in aqueous solution. They are often used as thickeners, emulsifiers, conditioners, flocculants, and even as drag reducers. Furthermore they are added to many foods and to concrete mixtures (superplasticizer). Some examples of polyelectrolytes which find applications in food products include pectin, carrageenan, alginate, polyvinylpyrrolidone and carboxymethylcellulose. Finally, they are also used in a variety of materials, including cement. Some of the applications of polyelectrolytes are presented in Tables 2.1 and 2.2.

**Table 2.1** Application of Some Natural Polyelectrolytes

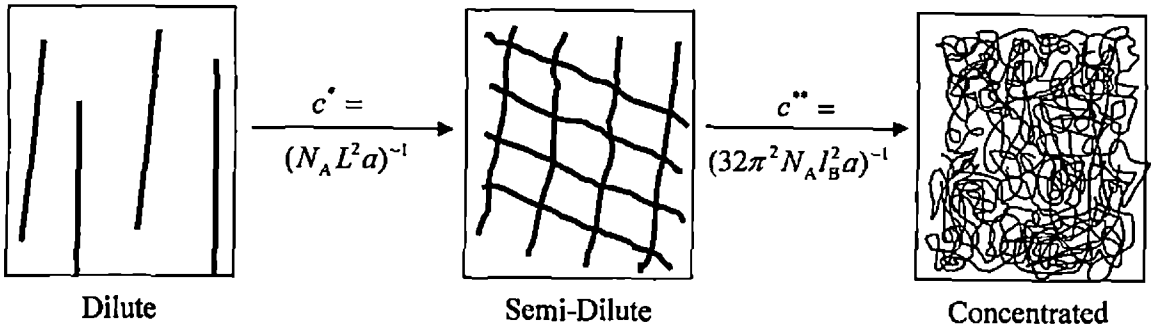
Polyelectrolytes	Applications
Pectin	Stabilizer for soft drinks
Alginate	Textiles, printing pastes, salad dressings
Carboxymethylcellulose	Sanitary use, paper industry
Carragenan	Thickening of food products
Chitosan	Membrane, pharmacy
Agar	Suspending agent BaSO <sub>4</sub> in radiology
Gum Arab	Thickener for ink and printing pastes

**Table 2.2** Application of Some Synthetic Polyelectrolytes

Polyelectrolytes	Applications
Poly-diallyldimethylammonium chloride	Water treatment, membranes
Polyethyleneimine	Paper industry
Polyamidamine	Sludge industry
Ionenex	Water treatment, membranes
Polyacrylic acid and copolymers	Water treatment, microcapsules
Maleic acid anhydride copolymers	Adhesive, paper industry
Polystyrenesulphonate	Membrane, drugs

#### 2.4. 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  $c^*$  ( $=1/N_A L^2 a$  where  $N_A$  = Avogadro number,  $L$  = contour length and  $a$  = length of a monomer unit). 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.<sup>14</sup> 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 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  $N_\xi$  correlation blobs of size  $\xi_0$ , each of them containing  $g$  monomers. Each blob bear an electric charge of  $q_\xi = z_c f e g$ .



**Figure 2.4** Concentration regime of polyelectrolyte solution

Because of the strong electrostatic interactions within each correlation blob, the chain is in 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 arguments<sup>15</sup> suggest polyelectrolyte behaviour similar to that of a neutral polymer 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  $\xi_0$  and Rouse-like dynamics for the stand of  $N/g$  beads of size  $\xi_0$ ). 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.<sup>16</sup> This evidence mostly stems from the study of non-equilibrium 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  $c_p$ . To arrive at the final conclusions as to the existence of these and other possible concentration regimes, more extensive experimental investigations and further theoretical efforts are required.

## 2.5 Properties of Polyelectrolyte Solutions: A Brief Review of Important Investigations

Despite the increasing theoretical and experimental efforts over the last 8-9 decades, the solution properties of polyelectrolytes are not yet well understood. Extensive reviews and entire books have been devoted to the properties of polyelectrolyte solutions<sup>16-32</sup> and no attempt is, therefore, 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 of 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.<sup>33-40</sup> 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.<sup>41</sup> At the same time Kagawa in Nagoya, Japan also started an independent program on polyelectrolytes. In his first paper on polyelectrolytes, Kagawa<sup>42</sup> introduced 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.<sup>16,24,31,43</sup> 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.<sup>16,19,24,25,31,43</sup> 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.<sup>2,31</sup>

The solvodynamic behaviour of polyelectrolyte molecules depends on their mass as well as on their 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.<sup>2</sup> 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.<sup>2,16</sup>

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.<sup>44</sup> 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 varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional

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coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.<sup>2,45,46</sup>

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.<sup>2,19</sup> 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.<sup>2,47-50</sup>

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.<sup>2</sup> 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.<sup>2,16,51-56</sup> 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<sup>55,56</sup> and the results indicated failure of the Manning and the Poisson-Boltzmann cell models. Later, Deserno *et al.*<sup>57</sup> 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.<sup>31</sup>

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

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the characterization of the molecular parameters of polyelectrolytes in solution.<sup>32,58-61</sup> For the past five 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 information, 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.<sup>62-66</sup> 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.<sup>64,67,68</sup> 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.<sup>69-72</sup> 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.<sup>73,74</sup>

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.<sup>75-82</sup>

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.<sup>2,83-85</sup>

It may be pointed out 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 test 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.*<sup>2</sup>

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 counterions<sup>86-93</sup> 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, could provide important information on the interactions between the polyions and the counterions and also on the conformation of the polyions in solution, from a more general point of view.

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 polystyrenesulphonate, an anionic polyelectrolyte, in 2-ethoxyethanol–water mixed solvent media. The effects of added salt and temperature have also been investigated.

## 2.6 Some Important Properties of Polyelectrolyte Solutions

### 2.6.1 Polyelectrolyte Conductance

#### 2.6.1.1 Manning Model for the Conductance of Salt-Free Polyelectrolyte Solutions<sup>19,94-98</sup>

The specific conductance and the equivalent conductivity,  $\Lambda$ , are two experimentally determined parameters which are suitable to describe the electrical transport properties of polyelectrolyte solutions because they 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<sup>19,94-98</sup> for dilute solutions of infinitely long linear polyionic chains.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by a linear charge density parameter defined by<sup>19,96,98</sup>

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

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 onto 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 the equivalent conductivity for a salt-free polyelectrolyte solution is related to  $\xi$  by the following equation<sup>95,96</sup>

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

where  $\lambda_c^0$  and  $\lambda_p$  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<sup>19,96,98</sup>

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

In contrast to Huizenga<sup>99</sup> 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,  $\lambda_p$  has been derived theoretically for the cylinder model of polyelectrolyte,<sup>97</sup> 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  $\eta_0$  being the coefficient of viscosity of the solvent. In Eq. (4),  $\kappa$  is the Debye screening constant, which is defined by

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

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

### 2.6.1.2 Limitation of the Manning Model

Since the Manning theory applies, as stated above, to highly diluted systems where polyion-polyion interactions are assumed to be absent and to polyions modelled 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 variation 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.*<sup>31</sup> and Wandrey and Hunkeler<sup>43</sup> 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 presented<sup>96</sup> 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 Hayes<sup>100</sup> and Szymczak *et al.*<sup>101</sup> 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 Hayes<sup>100</sup> studied the electrical conductances of lithium, sodium, potassium, cesium, magnesium, calcium, and strontium salts of polystyrenesulphonic 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  $7 \times 10^{-3}$  to  $1 \times 10^{-2}$  monomol·L<sup>-1</sup> for all counterions and the two investigated polyelectrolytes of molar masses of 70000 and 500000. 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 polystyrenesulphonic acid in semidilute solutions were carried out by

Szymczak *et al.* at 298.15 K.<sup>101</sup> 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.*<sup>102,103</sup> 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 bearing 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 rod-like structure of the polyion 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.<sup>104</sup>

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.<sup>92</sup>

Wandrey *et al.*<sup>105</sup> 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.*<sup>93</sup> compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4000 and 167000 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)], Rios<sup>106</sup> 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.

### 2.6.1.3 Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions<sup>107</sup>

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

In the semidilute solutions, the polyion chain is modelled as a random walk of  $N_\xi$  correlation blobs of size  $\xi_0$ , 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  $\xi_e$ . This means that for length scales less than  $\xi_0$ , the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size  $\xi_e$ ), and for length scales greater than  $\xi_0$ , the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size  $\xi_0$ .

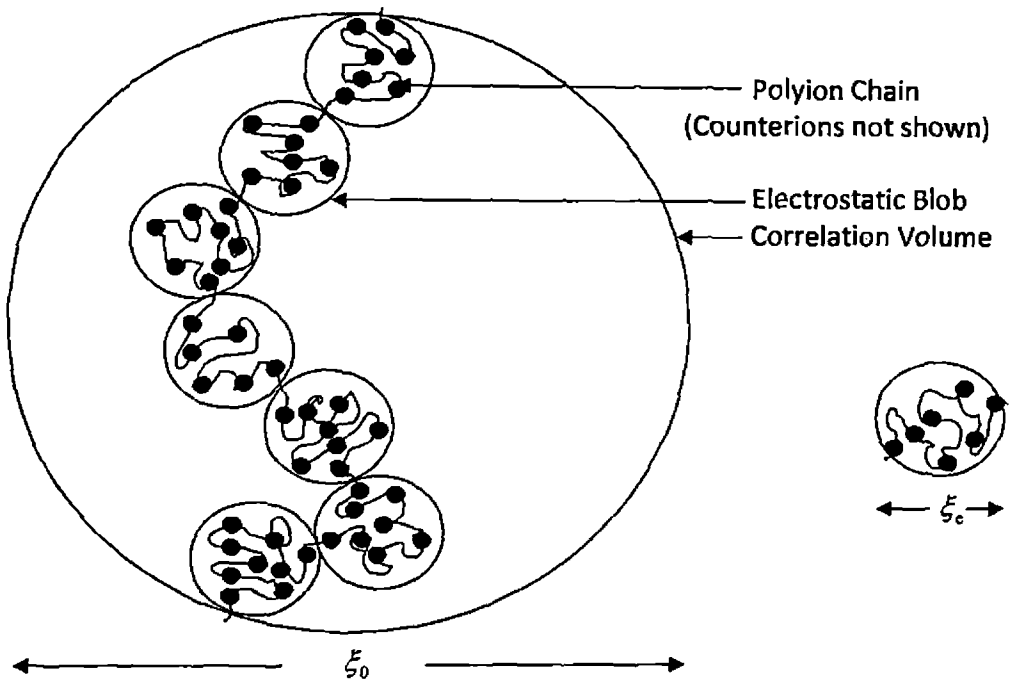
According to this model, in absence of an added salt, the equivalent conductivity of a polyion in a semidilute solution is given by

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

where  $F$  is the Faraday number and  $\eta_0$  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

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



**Figure 2.5** Schematic representation of correlation volume in a semidilute polyelectrolyte solution

The equivalent conductivity of a polyelectrolyte solution is then given by

$$\Lambda = f \left[ \lambda_c^0 + \frac{Fze^2 c \xi_0^2 \ln(\xi_0 / \xi_c)}{3\pi\eta_0} \right] \quad (9)$$

The above expression given by Colby *et al.*<sup>107</sup> is derived taking into account the scaling arguments proposed by Dobrynin *et al.*<sup>108</sup> 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  $f$ , 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 ( $\xi$ ), 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<sup>31,93,107</sup> and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify different concentration regimes with varying fractions of uncondensed counterions.<sup>109</sup> 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.<sup>110</sup>

#### 2.6.1.4 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.

Although the polyelectrolyte conductivities have been well-understood in salt-free solutions<sup>107</sup> using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*,<sup>108</sup> the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning<sup>110</sup> first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory<sup>95</sup> without much success. In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the "primitive additivity") of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.<sup>7-9,111,112</sup>

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 ( $\kappa$ ) of the polyelectrolyte in a salt solution through the equation,

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

where  $\kappa_p$  is the specific conductance of the polyelectrolyte in the absence of a simple salt and  $\kappa_s$  is the specific conductance of the simple salt in the absence of a polyelectrolyte.

However, these investigations<sup>7-9,111,112</sup> suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, Eq. (10).

Ander *et al.*<sup>111,112</sup> 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

$$\kappa = \kappa_p + \kappa_s \left( \frac{D_2}{D_2^0} \right) \quad (11)$$

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 co-efficients  $D_2/D_2^0$  has been used as a quantitative measure<sup>95</sup> of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be  $\kappa_s(D_2/D_2^0)$ .

Although the “modified” additivity has been shown to be somewhat better than the “primitive” one, departures from the experimental results are still prominent.<sup>111-115</sup> Later Bodri *et al.*<sup>116</sup> evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach<sup>108</sup> and compared them with the experimentally determined values. The agreement was rather good, although a quantitative description was not achieved.

Very recently, a simple approach has been put forward by us<sup>117</sup> to analyze the conductivity of polyelectrolyte solutions in the presence of an added electrolyte following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*<sup>107</sup> using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*<sup>108</sup>

Following Colby *et al.*,<sup>107</sup> the specific conductivity of a salt-free polyelectrolyte solution ( $\kappa_p$ ) is given by

$$\kappa_p = fc \left[ \lambda_c^0 + \frac{c\xi_0^2 e^2 f}{3\pi\eta_0} \ln \left( \frac{\xi_0}{\xi_c} \right) \right] \quad (12)$$

where  $c$  is the number density of monomers,  $\lambda_c^0$  the limiting equivalent conductivity of the counterions, the  $\eta_0$  the coefficient of viscosity of the medium.

The interactions between the polyion and the counterions will be modified in the presence of an electrolyte and this will result in different level of counterion condensation,

that is, in a different value of  $f'$  (designated as  $f'$ ). The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt can be expressed as

$$\kappa_{p(\text{eff})} = f'c \left[ \lambda_c^0 + \frac{c\xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left( \frac{\xi_0}{\xi_c} \right) \right] \quad (13)$$

Thus, the total specific conductivity ( $\kappa$ ) of a polyelectrolyte solution with added simple electrolyte should be equal to the sum of the specific conductivity of the simple salt in the absence of a polyelectrolyte and the effective specific conductivity due to the polyelectrolyte in the presence of a simple salt and is given by

$$\kappa = \kappa_s + f'c \left[ \lambda_c^0 + \frac{c\xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left( \frac{\xi_0}{\xi_c} \right) \right] \quad (14)$$

Eq. (14) has one adjustable parameter  $f'$ , and this could be obtained by the method of a least-squares fit of the experimental specific conductivity of the polyelectrolyte solution ( $\kappa$ ) in the presence of a salt to Eq. (14) using the measured specific conductance ( $\kappa_s$ ) of the salt in the absence of the polyelectrolyte. This value of  $f'$  takes care of the changed polyion-counterion interactions under the influence of the added salt. The second term in Eq. (14) is the actual contribution of the polyelectrolyte species toward the total specific conductivity in the presence of an added salt.

This approach has been extensively tested with data on sodium polystyrenesulphonate in the presence of sodium chloride in 2-ethoxyethanol–water mixed solvent media at different temperatures.<sup>117</sup> The data set used considered a number of parameters, for example, relative permittivity of the medium, temperature, and concentration of the added salt. Moreover, three decades of concentration of the polyelectrolyte were covered. Very good quantitative agreement with only one adjustable parameter has been observed.

Further support in favour of the validity of this new model has now been provided by another study on the electrical conductivity of sodium carboxymethylcellulose–NaCl solution in acetonitrile–water mixture.<sup>118</sup>

## 2.6.2 Polyelectrolyte Viscosity

### 2.6.2.1 Viscosity of Polyelectrolytes as a Function of Concentration

Viscosity is an important property for the determination of molecular structure and conformation of both neutral and charged polymers. In case of neutral polymer solutions, the

reduced viscosity  $\eta_{sp}/c_p$  (defined as  $\eta_{sp}/c_p = (\eta - \eta_0)/\eta_0 c_p$ , where  $\eta$  is the viscosity of the solution,  $\eta_0$  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  $\eta_{sp}/c_p$  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 polymer concentration. In these studies, which are summarized in the pioneering work of Fuoss,<sup>119,120</sup> a straight line is obtained when the reciprocal of the reduced viscosity is plotted as a function of the square root of the polymer concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the reciprocal of the intrinsic viscosity. However, careful investigation of the dilute solution behaviour revealed that the apparently unbounded increase of the reduced viscosity is invariably followed by a maximum,<sup>121-124</sup> and that normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. Thus, the method of Fuoss could not be used to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. 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.<sup>124</sup> The anomalous shape of the curve of the reduced viscosity versus concentration for dilute salt-free solutions, found in many studies during the last five 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.<sup>125</sup> Hodgson and Amis<sup>126,127</sup> 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,<sup>128,129</sup> poly (galacturonic acid) and its sodium salt,<sup>130</sup> sodium

polystyrenesulphonate,<sup>122,131</sup> sodium carboxymethylcellulose,<sup>132</sup> polysulphobetaines,<sup>133-136</sup> polyelectrolytes with poly(*p*-phenylene) backbone<sup>137</sup> 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.<sup>138</sup> Later Cohen *et al.*<sup>122,123</sup> derived a similar relation on the basis of the theory by Hess and Klein<sup>139</sup> 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.*<sup>140</sup> who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.<sup>141</sup> 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 electrostatic interaction and of conformational change of the polyion on experimental viscosity data.

In their approach Nishida *et al.*<sup>140</sup> 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.*<sup>142</sup> demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.<sup>139</sup> 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 Eqv·L<sup>-1</sup> and  $\kappa$  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 ( $\lambda$ ) is  $>1$  or  $\leq 1$ , 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  $\lambda$  is  $>1$  or  $\leq 1$ , respectively.

Antonietti *et al.*<sup>143</sup> expressed the reduced viscosity for charged latex particle as,

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

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.

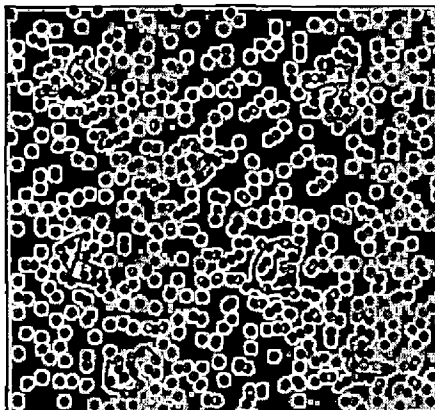
### 2.6.2.2 Intrinsic Viscosity

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.

### 2.6.2.3 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  $(\eta_{sp} / c_p)$  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<sup>2,144</sup>





**Figure 2.6** Elimination of polyelectrolyte effect by addition of a large excess of a salt

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

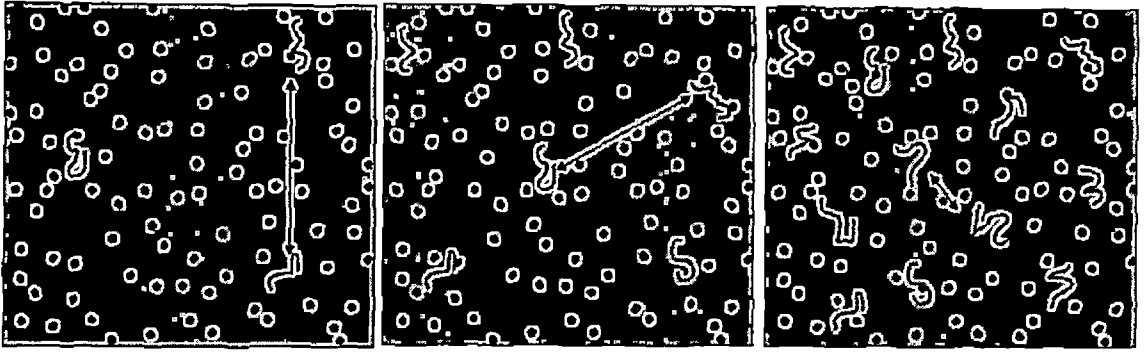
here  $k_H$  is the Huggins constant which is a characteristic for a given polymer-solvent system.

Addition of large excess of a salt into the polyelectrolyte solution causes partial or complete screening of interactions between the polyion chains. As a result, coiling of polyelectrolytes take place and thereby it behaves like uncharged polymer.

#### 2.6.2.4 Determination of Intrinsic Viscosity of a Polyelectrolyte by Isoionic Dilution

This is another method for the determination of the intrinsic viscosity of a polyelectrolyte.<sup>124,145</sup> 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 that of the original solution 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.*<sup>124,129,145,146</sup>



Isoionic Dilution

Figure 2.7 Dilution keeping fixed ionic strength

### 2.6.3 Partial Molar Volumes of Polyelectrolytes

The apparent molar volume ( $\phi_v$ ) 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,  $\rho$  the density of the solution and  $\rho_0$  the density of the solvent.

In majority of the polyelectrolyte solutions investigated, the apparent 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.<sup>147-152</sup> The insensitivity of the  $\phi_v$  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  $\phi_v$  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  $\phi_v$  values.<sup>153,154</sup>

The apparent molar volume at infinite dilution ( $\phi_v^0$ ) is equal to the partial molar volume ( $\bar{V}_2^0$ ) at zero concentration. In the literature, the partial molar volumes at infinite

dilution have usually been considered as the mean of the observed  $\phi_v$  values when these are independent of concentration, whereas the  $\phi_v^0$  values were determined by extrapolating  $\phi_v$  values to zero polyelectrolyte concentration when  $\phi_v$  values were found to depend upon the concentration.

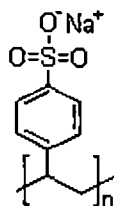
Limiting partial molar volume is an important thermodynamic property which may be helpful in elucidating the solute-solvent as well as solute-solute interactions. Moreover, this is also necessary for the application of characterization methods and physicochemical techniques including preparative and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

Various concepts concerning the electrostrictional hydration effect, the hydrophobic structural effect, and counterion-binding onto the polyion chain in polyelectrolyte solutions were interpreted on the basis of this property.<sup>147-150,155-157</sup> Empirical procedures have been developed to calculate and predict the limiting partial molar volumes for non-ionic and ionic organic compounds in aqueous solutions.<sup>158,159</sup> However, the evaluation of the limiting partial molar volumes by these procedures has not been attempted in mixed solvent media because of the lack of availability of reliable experimental molar volume data for a broad variety of polyelectrolyte in such solvents.

## 2.7 Present Investigation

From the above discussion, it is apparent that the problem of intra-polyion and polyion-counterion interactions is intriguing and, therefore, is not yet understood completely. It is thus desirable to address this problem using different experimental techniques to obtain an unambiguous picture of polyelectrolyte solutions. Moreover, to study the behaviour of polyelectrolyte solutions from a general point of view, investigations in mixed solvent media would be of great help 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. Considering these aspects we have, utilized three important methods *viz.*, conductometry, viscometry, and volumetry to study the behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixed solvent media with particular attention to various kinds of interactions involved.

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



**Figure 2.8** Structure of sodium polystyrenesulphonate

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. The dissertation aims to address, these aspects of polyelectrolyte solutions with particular reference to the system mentioned above.

Sodium polystyrenesulphonate (trade names Kayexalate, Kionex, Resonium A) is the sodium salt of polystyrenesulphonic acid (Figure 2.8). The polyanion is readily soluble in water, and insoluble in lower alcohols. The solid appears as white or off-white powder. This can be synthesised by several methods; recently it is reported that the 'atom transfer radical polymerization (ATRP)' of protected styrene sulphonates is one of the successful method,<sup>160,161</sup> leading to well defined linear polymer as well as more complicated molecular architectures.<sup>162</sup> In cement industry sodium polystyrenesulphonate is used as a superplasticiser. It is also used for dye improving agent for cotton and as proton exchange membranes in fuel cell applications. Sulphonated crosslinked polystyrenes are being used widely in ion-exchange applications. It also has its application in the medical science. To remove dangerously high levels of potassium in blood (since this causes cardiac arrhythmias and death), sodium polystyrenesulphonate (Kayexalate) is administered orally or rectally. It is also effective at reducing serum potassium levels,<sup>163</sup> although there is concern about possible side effects when it is mixed with sorbitol.<sup>164</sup> Due to the cationic exchange property, sodium polystyrenesulphonate is used successfully to bind plasma lithium caused by overdose in a victim.

In this study, 2-ethoxyethanol–water mixtures have been used as the solvent media. 2-Ethoxyethanol belongs to a class of compounds commercially known as cellosolves. It is, in fact, the monoethyl ether of ethylene glycol. Hence, it is very likely to show physico-

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chemical characteristics midway between protic and dipolar aprotic solvents. Simple consideration of molecular structures indicates that due to the presence of electron repelling  $\text{CH}_3\text{CH}_2-$  group, 2-ethoxyethanol is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of OH group makes 2-ethoxyethanol molecules less acidic than ethylene glycol and water, thus imparting a "quasi-*aprotic*" character to it. That is, it behaves as an amphiprotic dipolar solvent with low relative permittivity ( $D = 13.38$  at 298.15 K).<sup>165</sup> Moreover, it is completely miscible in water and the relative permittivities of the mixed solvent media could be varied over a wide range. Cellosolves find extensive use as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products.<sup>166,167</sup> Extensive investigations have, so far, been made on 2-ethoxyethanol as well as in its mixtures with water.<sup>168-180</sup> It would be, therefore, interesting to investigate the behaviour of a polyelectrolyte in these mixed solvents.

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