

## Chapter 2

### Introduction

Systems containing polyelectrolytes as well as their mixtures with electrolytes have been the subject of extensive investigation aimed at a fundamental understanding of their properties and evaluation of their use in various technical applications.

Coulombic interactions play a very important role in determining the behaviour of these systems. Since Coulombic (electrostatic) interaction energy varies inversely as the dielectric constant of the medium, these interactions can be altered simply by changing the composition of mixed solvent medium. Therefore, systems containing polyelectrolytes and those containing polyelectrolytes alongwith simple electrolytes can be studied from a more general point of view in mixed solvent media. Unfortunately, studies on polyelectrolyte-salt interactions in mixed solvent media are completely absent.

For a better understanding of the interactions between polyelectrolytes and electrolytes, a comprehensive investigation on systems containing both polyelectrolytes and electrolytes in mixed solvent media is, therefore, of utmost importance. An understanding of the behaviour of polyelectrolytes in these mixed solvent media is, of course, a prerequisite for this purpose.

The conformation of any polymer is affected by a number of factors: notably the polymer architecture and the solvent affinity. In the case of polyelectrolytes, charge also has an effect. Whereas an uncharged linear polymer chain is usually found in a random conformation in solution (closely approximating a self-avoiding three-dimensional random walk), the charges on a linear polyelectrolyte chain will repel each other (Coulomb interaction), which causes the chain to adopt a more expanded, rigid rod-like conformation.

This thesis, therefore, aims at elucidating (a) the behaviour of a selected polyelectrolyte and (b) the nature of its interactions with electrolytes in mixed solvent media using different experimental techniques.

In what follows, we will emphasize some of the important uses of different experimental techniques to unravel the behaviour of polyelectrolyte solutions with particular reference to various aspects of some of the thermodynamic and transport properties of these systems which will be followed by an account of the polyelectrolyte-salt interactions. Before

dealing with these aspects, an introduction to these important classes of compounds will be given.

### **Polyelectrolytes**

#### ***Definition of Polyelectrolytes***

The term polyelectrolyte denotes a class of polymeric species with 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 are proteins, nucleic acids, carrageenans, pectins, xanthan gum, carboxymethylcellulose etc. Under appropriate conditions in solution, the ionizable groups of polyelectrolyte molecules dissociate into polyions and a number of oppositely charged small ions commonly known as the counterions. The electrostatic interactions between the charged sites on the polyion chain and those of the surrounding counterions play a very important role in determining the behaviour of polyelectrolytes in solution. The conformations of polyelectrolytes in dilute solutions depend on the fraction of charged groups on the polyion and the ionic strength of the solution. For weakly charged polyelectrolytes (or macromolecules carrying a small percentage of ionizable groups), the roles of the non-Coulombic interactions such as van der Waals interactions, hydrogen bonding and other molecular interactions become important in governing the conformation of this kind of macromolecules. The behaviour of polyelectrolytes is also influenced by such factors as the solution pH, nature of the salt ions present, molecular weight, solvent polarity, temperature etc. Moreover the presence of the multiply-charged counterions significantly influences the structure and dynamics of the polyelectrolyte solutions.

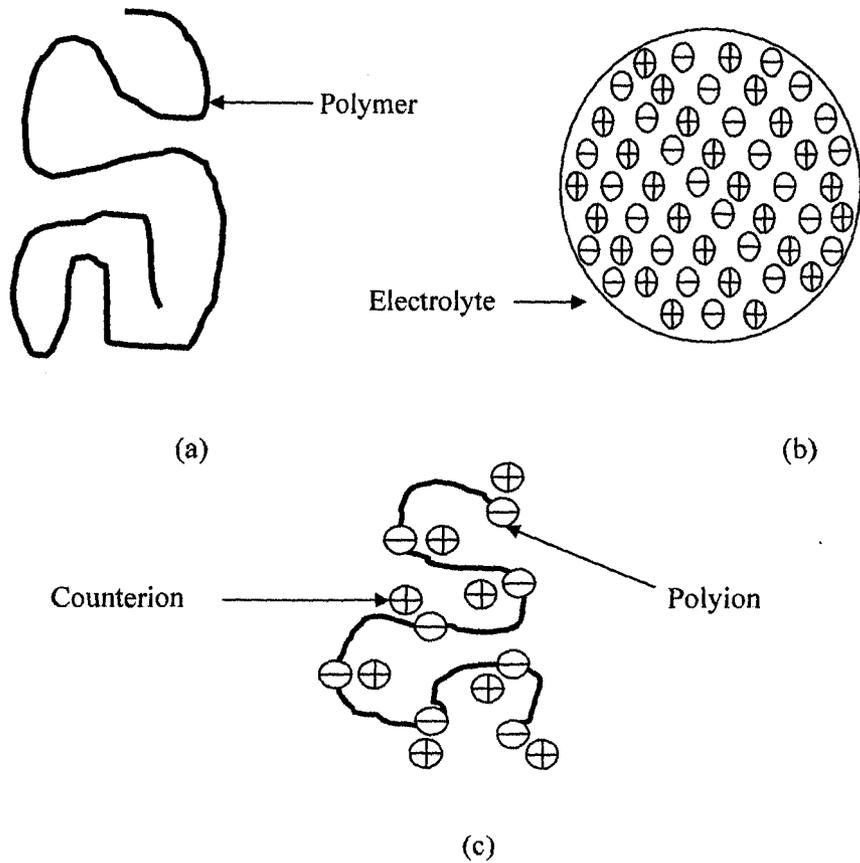
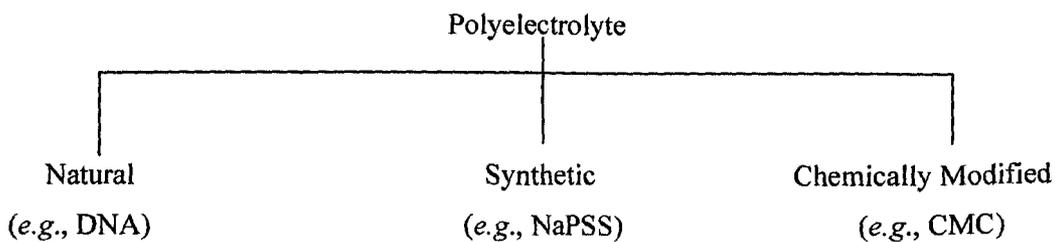


Fig. 1. (a) Polymer, (b) Electrolyte, and (c) Polyelectrolyte.

**Classification of Polyelectrolytes**

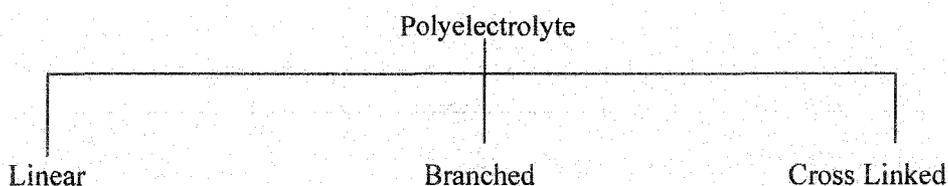
Polyelectrolytes can be classified in different ways. It is possible to distinguish between natural, synthetic and chemically modified natural polyelectrolytes. For example, deoxyribonucleic acid (DNA) is a natural polyelectrolyte, sodium polystyrenesulfonate (NaPSS) is a synthetic polyelectrolyte, and sodium carboxymethylcellulose is a chemically modified natural polyelectrolyte.



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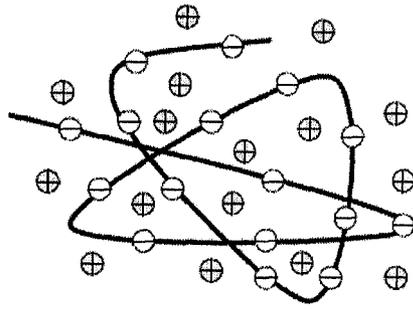
Polyelectrolytes may be grouped into linear, branched and cross-linked chains or into homo and copolymers. A polyelectrolyte could be a polyacid, a polybase or a polyampholyte depending upon whether the ionizable groups are all anionic, cationic or a mixture of both. Another distinction is also possible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

Depending upon their 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.

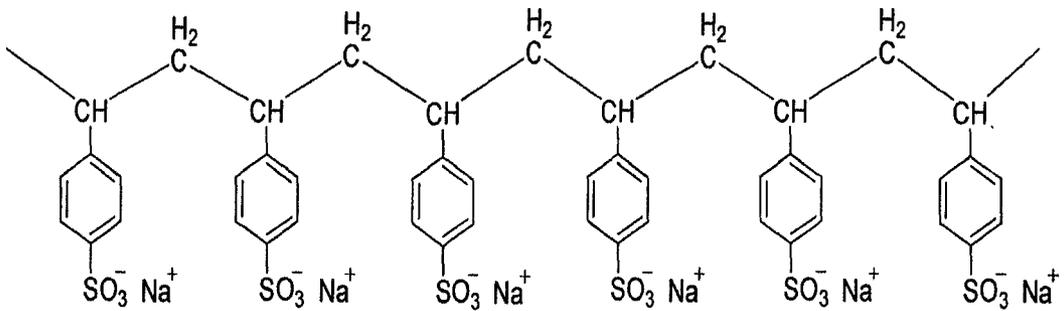


Although in a topological sense the backbone is linear, the shape of the polyelectrolyte might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.<sup>1</sup> Branched polyelectrolytes do not have linear chains and are less investigated species compared to the linear ones.<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>

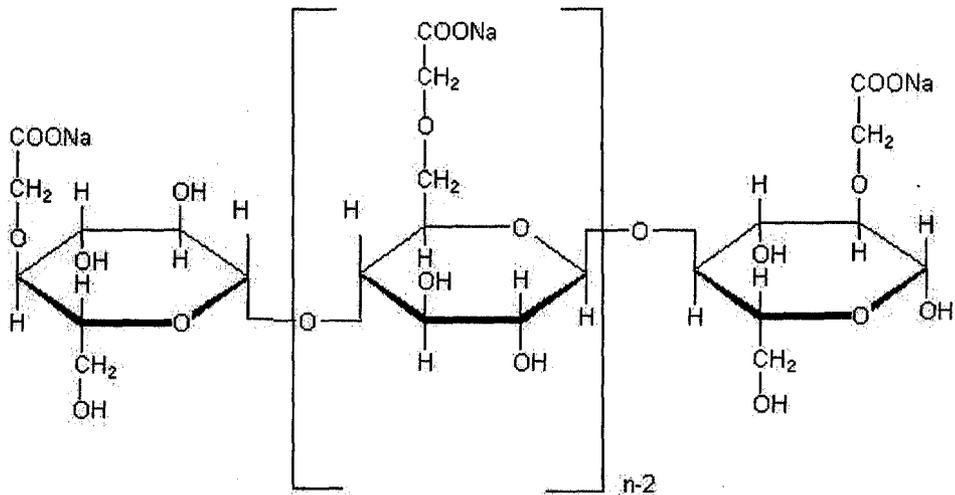
Polyelectrolytes could also be distinguished depending upon their conformations. Flexible polyelectrolytes (Figs. 1 and 2) comprises of a polyion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic 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 (Fig. 2). Rigid rod-like polyelectrolytes (Figs. 3 and 4) on the other hand, contains a polyion 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 (Fig. 4). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as DNA, ribonucleic acid (RNA) and the tobacco-mosaic virus.



**Fig. 2.** Schematic representation of a flexible polyelectrolyte.



**Fig. 3.** An example of a flexible polyelectrolyte: sulphonated polystyrene with sodium counterions.

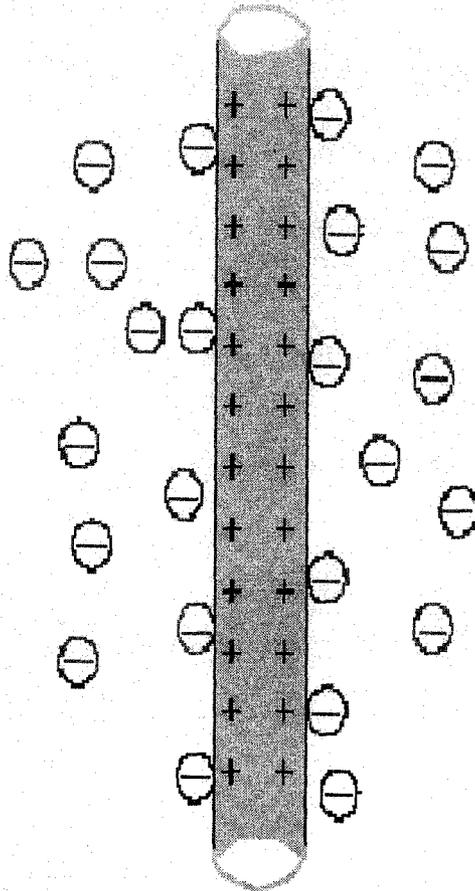


**Fig. 4.** Sodium carboxymethylcellulose with a degree of substitution of 1.

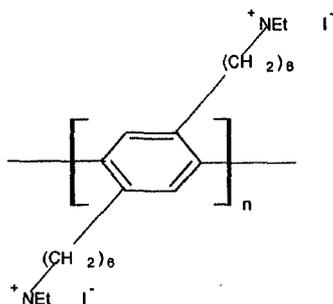
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*Importance of Polyelectrolytes*

Polyelectrolytes play an important role in molecular biology and materials science. For instance, some selected 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 pivotal role in maintaining and propagating life in the simplest as well as in the 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.



**Fig. 5.** Schematic representation of a stiff polyelectrolyte



**Fig. 6.** A rigid rod-like polyelectrolyte: 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 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 a 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.

### **Behaviour of Polyelectrolytes in Solutions**

#### ***Concentration Regimes in Polyelectrolyte Solutions***

The properties of polyelectrolytes in solution depend substantially upon their concentrations. There are three different concentration regimes in polyelectrolyte solutions. They are dilute, semidilute and concentrated regions. These could be understood from the concept of overlap concentration ( $c^*$ ) defined as the concentration where the polymer chains start to overlap. A dilute polymer solution refers to the concentration region ( $c < c^*$ ) where the polymer chains are well separated and do not interact with their neighbours. In such solutions, polyelectrolytes have a large overall size and a rather rigid local conformation.<sup>14</sup> The chain is represented by an extended rod-like configuration of  $N_D$  electrostatic blobs of

diameter  $D$  in the dilute regime. Each of them, with  $g_e$  monomers, carries a charge of  $q_D = z_c f e g_e$ , where  $z_c$  is the counterion valence,  $e$  the electronic charge, and  $f$  the fraction of ionized charged groups on the polyion chain (*i.e.*, the fraction of uncondensed counterions). With the increase in the polyelectrolyte concentration, the polyion chains become more flexible. When  $c < c^*$ , the chains begin to overlap and the conformations of the single chains are greatly modified. This region is known as the semidilute regime. The polyion chain is modelled as a random walk of  $N_\xi$  correlation blobs of diameter  $\xi_0$ , each containing  $g$  monomers in semidilute solutions. Each blob carries an electric charge of  $q_\xi = z_c f e g$ . Because of strong electrostatic interactions within each correlation blob, the chain is in a 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). The electrostatic blobs begin to overlap in much higher concentrations, and owing to the increase in electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments<sup>15</sup> suggest a polyelectrolyte behaviour similar to that of a neutral polymer solution.

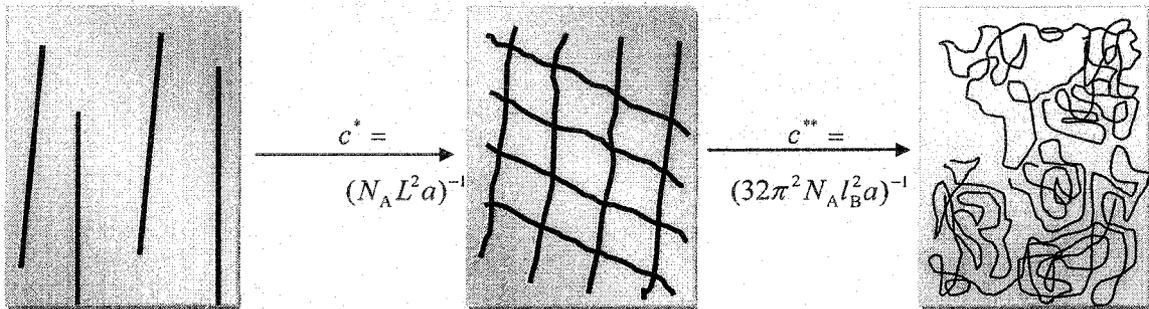


Fig. 7. Concentration regimes in polyelectrolyte solutions.

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 solvodynamic 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 strand of  $N/g$  beads of size  $\xi_0$ ). In short, a polyelectrolyte solution

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behaves as a concentrated solution for  $c > c_D$ , as an entangled-semidilute solution for  $c_e < c < c_D$ , as an unentangled-semidilute solution for  $c^* < c < c_e$ , and finally as a dilute solution for  $c < c^*$ . The available experimental evidences confirm 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 nonequilibrium properties, such as viscosity, conductance, or diffusion. Experiments are difficult to perform below the overlap concentration because of the very low concentrations and subsequently very small 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  $c_D$  and  $c^*$ . More extensive experimental investigations and further theoretical efforts are, therefore, required to arrive at the final conclusions as to the existence of these and other possible concentration regimes.

### **Brief Review of Some Important Investigations on Polyelectrolyte Solutions**

Despite the continuous experimental and theoretical efforts over the last 7-8 decades, the solution properties of polyelectrolytes are yet to be fully understood. There are extensive reviews and entire books on the properties of polyelectrolytes in solutions<sup>16-32</sup> and no attempt will, therefore, be made here to provide a comprehensive review of the vast literature which exists on this subject.

The early studies on synthetic polyelectrolytes have been reported in the 1930s.<sup>33-40</sup> The beginning of systematic investigations on polyelectrolytes, however, is dated back to the mid-1940s, when a study was initiated by Katchalsky at the Weizmann Institute, Israel<sup>41</sup> and at the same time, a research program was launched under the sponsorship of the Office of Naval Research at Yale, USA. At that time Kagawa in Nagoya, Japan also started an independent program on polyelectrolytes. In the first paper on polyelectrolytes, Kagawa<sup>42</sup> introduced the important concept of counterion binding in understanding the characteristic physicochemical properties of polyelectrolytes, *e.g.*, the dissociation constant and counterion activity.

Since the beginning of polyelectrolyte research, electrochemical methods have been employed as powerful tools to investigate and analyze the equilibrium properties and the transport phenomena<sup>16,24,31,43</sup> of polyelectrolytes. The availability of the sophisticated

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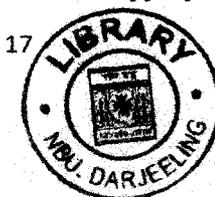
equipments in conjunction with the development of advanced theoretical approaches, contributed to the increasing significance of potentiometry and conductometry to explore the polyion-counterion interactions and to a better fundamental understanding of polyelectrolyte solution properties.

Solution behaviour of the polyelectrolytes have also been studied by various transport properties such as viscosity, sedimentation, diffusion, and electrophoresis.<sup>16,19,24,25,31,43</sup> Moreover, dielectric spectroscopy, osmometry 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 a third component, for example a salt, which influences the conformation of the macroions. Besides the scattering methods, viscometry offers the possibility of studying conformational changes of polyelectrolytes, in particular, the influence of the ionic strength on the molecular dimension.

Viscosity is a property of the solution under the influence of a mechanical perturbation. On the other hand, diffusion phenomena are directly related to the relative motion of solute particles in a stationary system. Various kinds of isothermal diffusion may be distinguished, associated with 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. Diffusional fluxes, on the other hand, 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> Diffusion of electroneutral components takes place in the presence of macroscopic concentration gradients. Diffusion is observed on the macroscopic scale where electroneutrality is observed locally. However, 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 ionic 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 on the properties of salt-free polyelectrolyte solutions, but no appropriate theoretical approaches and



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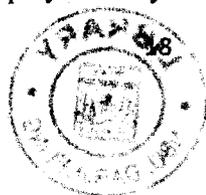
experimental investigations are available at present, which allows the use of sedimentation measurements in this respect.<sup>44</sup> However, in presence of sufficiently high amounts of supporting low molar mass electrolytes, the motion of the polyions and the counterions is largely decoupled and ultracentrifugation 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 coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.<sup>2,45,46</sup>

Gel electrophoresis has been a well-established and successful tool in separation and analysis of biopolymers, especially proteins for a long time. Information as to the dependences of the polyion electrophoretic mobility on the gel concentration, electric field strength, chain length, ionic strength, charge density etc. can be obtained from electrophoresis studies.<sup>2,47-50</sup> But the gel electrophoretic studies for synthetic polyelectrolytes are relatively scarce.<sup>2,19</sup>

All of the commonly measured colligative properties of simple ionic solutions *e.g.*, Donnan equilibrium, osmotic pressure 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 to estimate the fractions of uncondensed counterions. In the literature,<sup>2,16,51-56</sup> substantial amount of information on the osmotic coefficients and the Donnan equilibria of polyelectrolytes is available. Moreover, several investigations on the osmotic coefficients of a synthetic rod-like (rigid) polyelectrolyte solutions have also been performed to test various models of polyelectrolyte solutions describing the electrostatic interactions of the counterions with the polyion<sup>55,56</sup> and the results clearly demonstrated the failure of the Manning and the Poisson-Boltzmann cell models. Afterwards, an analysis performed by Deserno *et al.*<sup>57</sup> on 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 concluded that they indeed give a good description of the influence of the correlations of the counterions with the polyion.

The dielectric properties of aqueous solutions of polyelectrolytes present a very complex phenomenology, not yet understood completely. The century-old dielectric methods are still one of the most important techniques for studies on the structure and dynamics of polymer solutions. This is due to the capability of these methods to investigate the relaxation processes occurring in aqueous polyelectrolyte solutions in an extremely wide range of

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characteristic times, approximately from  $10^{-12}$  through  $10^3$  s. Information on the effective charge on the polyelectrolyte chains, the fraction of condensed counterions, and the effective friction coefficient of condensed counterions, can be obtained from dielectric spectroscopic techniques.<sup>31</sup>

Static light scattering (SLS), small-angle X-ray scattering (SAXS), and small angle neutron scattering (SANS) are classical scattering methods, and are of special importance in the characterization of the molecular parameters of polyelectrolytes in solution.<sup>32,58-61</sup> There has been an increasing interest in dynamic scattering methods, particularly dynamic light scattering (DLS) for the past four decades, 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.

The main focus of light scattering studies on polyelectrolyte solutions was, up to about 1980, on the coil expansion and the second virial coefficient as a function of the ionic strength of the medium, besides their role in routine determination of 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 or in very dilute salt solutions. Compared to the static 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> For the characterization of biopolymers, such as proteins and nucleic acids, SAXS plays a very important role. 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 conjunction with, for instance, SLS and DLS, 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 on 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 concentration, ionic strength, and molecular mass.<sup>2,83-85</sup>

Although the experimental data obtained from different scattering methods regarding the intermolecular structure factor of semidilute salt-free polyelectrolyte solutions are qualitatively in good agreement, quantitative discrepancies occur and the real structure models are still unclear. To verify the theoretical models in more details, comprehensive and sophisticated experiments are necessary. A brief and very useful review on the application of these different scattering techniques is available in Dautzenberg *et al.*<sup>2</sup>

Even if 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 polyelectrolyte behaviour from a more general point of view. Studies in such systems, hence, could provide important insight into the fundamental understanding of the interactions between the polyions and the counterions and also on the conformation of the polyions in solution.

Here, we shall dwell upon different aspects of transport and thermodynamic properties of a selected anionic polyelectrolyte sodium carboxymethylcellulose in methanol-water mixed solvent with particular attention to the variation of counterion condensation, polyion-counterion interaction, and polyion conformation.

### **Some Important Properties of Polyelectrolyte Solutions**

#### ***Polyelectrolyte Conductance***

The specific conductance and the equivalent conductivity ( $\Lambda$ ) are two experimentally determined parameters which conveniently describe the electrical transport properties of polyelectrolyte solutions because they take into account the movement of any charged species present in the solutions under the influence of an externally applied electric field.

***Salt-Free Polyelectrolyte Solutions: The Manning Counterion Condensation Model***

Manning counterion condensation theory<sup>19,94-98</sup> forms the basis for the description of different electrical properties of polyelectrolytes in dilute solutions assuming counterion condensation for an infinitely long and thin line charged chain.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by<sup>19,94-98</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  $\xi > 1$ , sufficient number of counterions condense onto the polyion to give the critical value  $\xi = 1$ . If, on the other hand,  $\xi < 1$ , ionization takes place to reach this critical value. A limiting law for the equivalent conductivity of 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 the parameter  $f$  is given by<sup>19,96,98</sup>

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

Contrary 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 the condensed counterions, certainly can be considered as bound, the fraction of such ions being

$1 - \xi^{-1} \neq 1 - f$ , while 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 the contributions due to electrophoretic and relaxation effects to the equivalent conductivity, the polyion equivalent conductivity  $\lambda_p$  was derived theoretically for the cylinder model of polyelectrolytes,<sup>97</sup> and for counterions with a charge of  $z_c$  it can be expressed as

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

where the parameter  $a$  is the radius of the assumedly cylindrical polymer chain, while

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

with  $\eta_0$  being the coefficient of viscosity of the solvent. In Eq. (4),  $\kappa$  is the Debye screening constant defined by

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

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

### ***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 modeled as a linear array of point charges, its validity is restricted to very low concentration regimes of polyelectrolyte solutions.

Previous studies indicated that although within a limited concentration range, the concentration dependence of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not, in general, 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 detailed review of the vast literature that exists on this subject. However, some of the important results will be discussed 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 polyelectrolyte concentration was published in 1975. Quite 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 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  $7 \times 10^{-3}$  to  $1 \times 10^{-2}$  monomol.L<sup>-1</sup> for all counterions and for the two investigated polyelectrolytes with 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 subsequent increase beyond the minimum could not be accounted for. It was concluded that the applicability of the Manning theory is questionable for a concentration range where the polyion chain tends to coil. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonic 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 investigated. They suggested that the Manning theory for electrical transport properties might require additional theoretical considerations.

Other studies by 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 with 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 conductivity behaviour of dextran

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sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rodlike structure on which the theory is based.

Large 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 equivalent conductivity of aqueous tetra-*n*-alkylammonium salts of pectic acid above and below the overlap concentration also manifested large deviation from the Manning limiting law.<sup>92</sup>

Wandrey<sup>105</sup> made extensive use of the Manning model for conductivity of dilute and semidilute polyelectrolyte solutions in inert atmospheres and pointed out deviations from the model predictions.

Bordi *et al.*<sup>93</sup> measured the equivalent conductances of poly (*L*-lysine) samples with molar masses of 4,000 and 167,000 for both the dilute and semidilute regimes, and compared their results with the predictions according to the Manning model. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polyelectrolyte molar mass. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molar mass sample is not surprising, since the polyelectrolyte concentrations data are all above  $c^*$ , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molar mass sample is especially noteworthy since these data are all below  $c^*$  where the Manning model should, in principle, apply.

The study by Rios<sup>106</sup> on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-*co*-(vinyl pyrrolidone)], Rios<sup>106</sup> paid 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 experimentally observed in each of these three cases. The agreement between the experiment and theory is generally poor; the theoretical curves are, however, found to approach the experimental ones for the lithium and sodium salts over a very narrow concentration range in very dilute solutions.

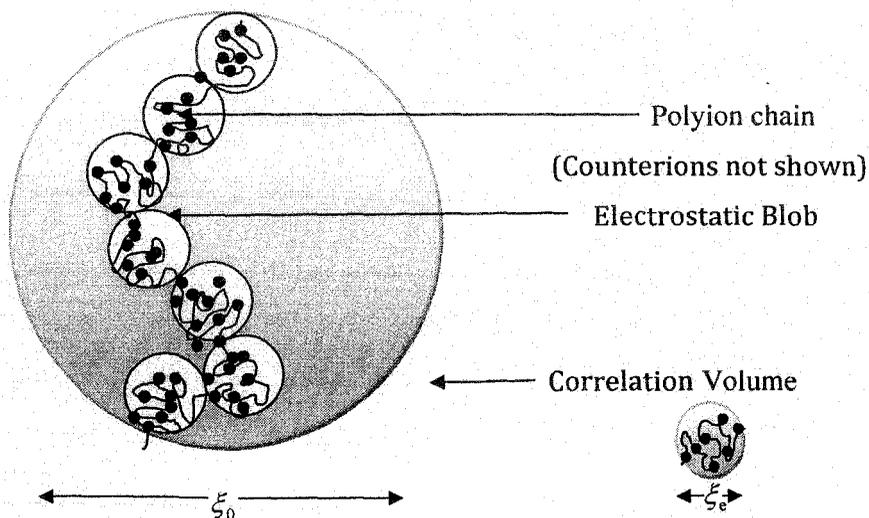
The inadequacy of the Manning model to describe the conductivity behaviour of solutions of sodium carboxymethylcellulose and sodium polystyrenesulfonate in aquo-organic mixed solvent media has also been reported.<sup>107-111</sup>

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

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**Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions**

A successful model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*<sup>112</sup> using the scaling description proposed by Dobrynin *et al.*<sup>113</sup> for the configuration of a polyion chain. In the semidilute solutions, the polyion chain is modeled as a random walk of  $N_\xi$  correlation blobs of diameter  $\xi_0$ , each of them containing  $g$  monomers. Each blob bears an electric charge of  $q_\xi = zefg$  ( $z$  being the counterion valence,  $e$  the electronic charge and  $f$  the fraction of uncondensed counterions) 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 diameter  $\xi_e$ . 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 diameter  $\xi_e$ ), and for length scales greater than  $\xi_0$ , the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of diameter  $\xi_0$ . Within this model, in absence of an added electrolyte, the equivalent conductivity can be calculated by an equation.



**Fig. 8.** Schematic diagram of correlation volume in a semidilute polyelectrolyte solution.

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 constant and  $\eta_0$  is the coefficient of viscosity of the medium.

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 monomer number density) 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

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

The above expression was derived by Colby *et al.*<sup>112</sup> taking into account the scaling arguments proposed by Dobrynin *et al.*<sup>113</sup> neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. It may be seen from Eq. (9) that the above model relies on 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 polyelectrolyte concentration given by the value of the charge density parameter  $\xi = \lambda_B/b$ , Eq. (9), can be applied to more concentrated systems, up a concentration of  $c_D$ , where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This model has been applied, so far, to a limited number of aqueous polyelectrolyte systems<sup>31,93,112,114</sup> 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.<sup>115</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 and sodium carboxymethylcellulose in methanol-water mixed solvent media.<sup>110,111</sup>

### *Effect of Salts on the Conductance of Polyelectrolyte Solutions*

Although the polyelectrolyte conductivities have been well understood in salt-free semidilute solutions<sup>112,114</sup> in the light of the scaling description for the configuration of a polyion chain in accordance with Dobrynin *et al.*,<sup>113</sup> the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions. Devore and Manning<sup>116</sup> were the first to make an attempt to describe the electric transport properties of polyelectrolyte solutions in presence of 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>117-121</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 by adding the value of specific conductance of salt and polyelectrolyte. The equation is

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

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 polyelectrolyte.

However, earlier investigations<sup>117-121</sup> suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not generally agree with those predicted by simple additivity, Eq. (10).

Later Kowblansky and Ander<sup>117</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

$$\kappa = \kappa_p + \kappa_s (D_2 / D_2^0) \quad (11)$$

where  $D_2$  and  $D_2^0$  are the coion 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<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 superior to the “primitive” one, the departures from the experimental results are not yet accounted for.<sup>117-121</sup> Later, Bordi *et al.*<sup>122</sup> evaluated the equivalent conductances for a hydrophilic polyion with a salt in the light of scaling theory approach<sup>113</sup> and compared them with their experimental results. The agreement is rather good, although a quantitative description is still awaited.

Very recently, one of us has introduced<sup>123</sup> a simple approach to analyze the conductivity of semidilute polyelectrolyte solutions in the presence of an added electrolyte based on the scaling theory for the conductivity of semidilute polyelectrolyte solutions neglecting the asymmetry field effect.<sup>112</sup> This new model has been extensively tested with data on (i) sodium polystyrenesulfonate-sodium chloride system in 2-ethoxyethanol-water mixed solvent media,<sup>123</sup> and (ii) sodium carboxymethylcellulose-sodium chloride system in acetonitrile-water mixed solvent media<sup>124</sup> considering a number of parameters *e.g.*, temperature, relative permittivity of the medium, and concentration of the added salt. Very good quantitative agreement with only one adjustable parameter has been achieved. A brief description of this model is given below.

According to Colby *et al.*,<sup>112</sup> the specific conductivity of a salt-free polyelectrolyte solution ( $c$ ) neglecting the asymmetry field effect is given by

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

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where  $\lambda_c^0$  is the limiting equivalent conductivity of the counterions,  $c$  the number density of monomers, and  $\eta_0$  the coefficient of the viscosity of the medium. Here, the term  $f$ , the fraction of uncondensed counterions, also provides a measure of polyion-counterion interaction in the absence of an electrolyte.

The interactions between the polyion and the counterions would, obviously, be altered in the presence of an electrolyte and this would result in a different level of counterion condensation, *i.e.*, in a different value of  $f$  and will be designated as  $f'$ . The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt  $\kappa_{p(\text{eff})}$  can then be expressed as

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

The total specific conductivity of a polyelectrolyte solution with added simple electrolyte should, thus, 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 the simple salt

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

In the above equation,  $f'$  has been treated as an adjustable parameter and this can be conveniently obtained by the method of a least-squares fit of the experimental specific conductivity of the polyelectrolyte solution ( $\kappa$ ) in presence of a salt to Eq. (14) provided  $\kappa_s$  is known. 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 towards the total specific conductivity in the presence of an added salt.

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### Polyelectrolyte Viscosity

#### *Viscosity of Polyelectrolytes as a function of Concentration*

Viscosity is an important tool for the determination of molecular structure and conformation of both neutral and charged polymers. Polyelectrolyte solution viscosity depends very much not only on the chemical structure of the polyion, its size and charge density, but also on the environmental properties such as the ionic strength and the solvent polarity.<sup>125-136</sup> In case of neutral polymer solutions, the reduced viscosity  $\eta_{sp}/c$  (defined as  $\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$ , where  $\eta$  is the viscosity of the solution,  $\eta_0$  is the viscosity of the solvent alone and  $c$  is the (monomer) concentration of the polyelectrolyte solution) is proportional to  $c$ . This well-known relation (known as the Huggins equation<sup>2</sup>) is used for determining the intrinsic viscosity  $[\eta]$  simply by extrapolation of  $\eta_{sp}/c$  values to  $c = 0$ . On the other hand, salt-free polyelectrolyte solutions exhibit an anomalous dependence of viscosity on concentration. Early investigations on the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that reduced viscosity would increase monotonically as the polyion concentration is reduced. In these studies, which are summarized in the pioneering work of Fuoss,<sup>125,126</sup> a straight line is obtained when inverse reduced viscosity is plotted as a function of the square root of the polymer concentration. It is usually assumed that this straight line could be extrapolated to zero concentration and that the intercept at zero polyelectrolyte 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 always followed by a maximum,<sup>127-130</sup> 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.<sup>130</sup> The anomalous shape of the curve of the reduced viscosity versus concentration for dilute salt-free solutions, found in many studies, was generally interpreted as the result of expansion and contraction of the flexible polyion due to short-range interactions. Most of these investigations were performed on weak polyelectrolytes e.g., derivatives of polyvinylpyridine and polymers containing carboxylic acids, as reviewed by Tanford.<sup>131</sup> Hodgson and Amis<sup>132,133</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>134,135</sup> poly (galacturonic acid) sodium salt,<sup>136</sup> sodium polystyrenesulfonate,<sup>128,137</sup> sodium carboxymethylcellulose,<sup>138</sup> polysulfobetaines,<sup>139-142</sup> and polyelectrolytes with poly(*p*-phenylene) backbone<sup>143</sup> etc.

In 1987 Witten and Pincus put forward a theory for the viscosity of polyelectrolyte solutions which was derived for solutions near the overlap concentration.<sup>144</sup> Later Cohen *et al.*<sup>128,129</sup> derived a similar relation on the basis of the theory by Hess and Klein<sup>145</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, despite 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>146</sup> who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.<sup>147</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 interaction and of conformational change of the polyion on the experimental viscosity data.

In their approach Nishida *et al.*<sup>146</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>148</sup> demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.<sup>145</sup> On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard

spheres in the presence of a salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following equation,

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

where  $c$ , the polyelectrolyte concentration is expressed in Eqv.L<sup>-1</sup> and  $\kappa$  is the inverse Debye screening length.

Now, since  $\kappa^2 = 4\pi l_B(c + c_s)$  or  $\kappa^2 = 4\pi l_B(c/\xi + 2c_s)$  when the charge density parameter ( $\xi$ ) is  $>1$  or  $\leq 1$ , respectively, we can write

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

$$c/(c + 2c_s)^{3/2} \quad (17)$$

when  $\xi$  is  $>1$  or  $\leq 1$ , respectively.

Antonietti *et al.*<sup>148,149</sup> expressed the reduced viscosity for charged latex particles as:

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

in which  $(\eta_{sp}/c)_{HK}$  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. Antonietti *et al.*<sup>148</sup> observed that although a quantitative fit according to Eq. (18) could describe the polyelectrolyte behaviour in acetone, isopropyl alcohol, and ethanol, it was impossible to extract qualitative information, since each parameter value is rather unstable.

### ***Intrinsic Viscosity***

In discussing the conformation of single polymer chain from viscometric data, information about the intrinsic viscosity  $[\eta]$  is indispensable. Moreover, this parameter also

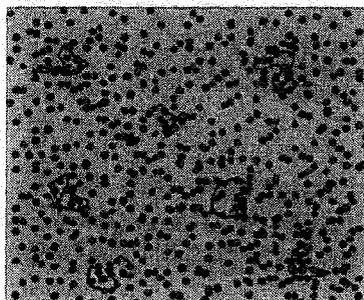
plays an important role in the molecular mass determination of polymer. For salt-free and low salt-containing polyelectrolyte solutions, however, the determination of this parameter presents a great challenge due to the anomalous concentration dependence of viscosity of polyelectrolyte solutions in these 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  $\eta_{sp}/c$  varies linearly with the polymer concentration ( $c$ ) 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>2,150</sup>

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

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



**Fig. 9.** Elimination of polyelectrolyte effect by addition of a large excess of a salt.

#### ***Determination of Intrinsic Viscosity of a Polyelectrolyte by the Method of Isoionic Dilution***

The intrinsic viscosities can be determined in a more straightforward manner using the method of isoionic dilution.<sup>130,151</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 manner that after each addition, the total ionic strength of the solution remains the same and equal to the initial

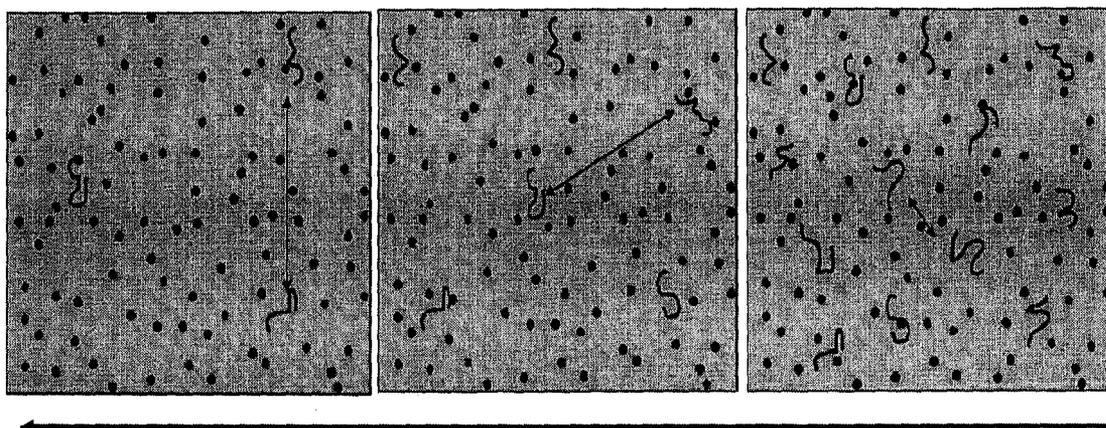


Fig. 10. Schematic representation of isoionic dilution.

value due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these conditions the reduced viscosity exhibits a linear decrease as one lowers the polyelectrolyte concentration and hence 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 isoionic dilution method for the determination of intrinsic viscosity in a convenient manner, however, very little attention has been paid to this direction so far.<sup>130,135,151-154</sup>

#### ***Determination of Intrinsic Viscosity of a Polyelectrolyte by Wolf Method<sup>155</sup>***

Recently Wolf<sup>155</sup> presented a new method for the determination of  $[\eta]$  based upon the application of the laws of phenomenological thermodynamics to the viscosity of polymer solutions and introduced a generalized intrinsic viscosity enabling a comparison of differently charged and uncharged polymers.

As long as the viscosity  $\eta$  of the solutions constitutes a variable of state, the intrinsic viscosity  $[\eta]$  is given by the initial slope of the dependence of the natural logarithm of the

relative viscosity  $\ln \eta_{rel}$  ( $\eta_{rel}$  = viscosity of the solution/viscosity of the solvent) on polymer concentration  $c$  (mass/volume). Under these conditions one can write

$$d \ln \eta = \left( \frac{\partial \ln \eta}{\partial c} \right)_{T,p,\gamma} dc + \left( \frac{\partial \ln \eta}{\partial T} \right)_{c,p,\gamma} dT + \left( \frac{\partial \ln \eta}{\partial p} \right)_{c,T,\gamma} dp + \left( \frac{\partial \ln \eta}{\partial \gamma} \right)_{c,T,p} d\gamma \quad (20)$$

This equation describes the relative change of  $\eta$  as a function of concentration  $c$  (mass per volume), temperature  $T$ , hydrostatic pressure  $p$ , and shear rate  $\gamma$  and enables the introduction of a *generalized* intrinsic viscosity  $\{\eta\}$  according to

$$\left( \frac{\partial \ln \eta}{\partial c} \right)_{T,p,\gamma} = \{\eta\} \quad (21)$$

The intrinsic viscosity itself can then be defined as

$$\lim_{c \rightarrow 0, \gamma \rightarrow 0} \left( \frac{\partial \ln \eta}{\partial c} \right)_{T,p,\gamma} = \lim_{c \rightarrow 0, \gamma \rightarrow 0} \{\eta\} = [\eta] \quad (22)$$

$[\eta]$  represents the specific hydrodynamic volume of *isolated* polymer coils, in contrast to  $\{\eta\}$ , which quantifies the specific hydrodynamic volume at a given polymer concentration  $c$ . The second and the third terms on the right hand side of Eq. (20) yield respectively the activation energy and the activation volume of the viscous flow, and the fourth quantifies the shear influences on  $\eta$ . This approach has, so far, been successfully applied by the Wolf group to a number of polyelectrolyte systems.<sup>155-158</sup>

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**Partial Molar Volumes of Polyelectrolytes**

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

$$\phi_v = \frac{M}{\rho} + 1000 \frac{(\rho - \rho_0)}{m\rho\rho_0} \quad (23)$$

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 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.<sup>159-164</sup> In the former cases, the partial molar volumes at infinite dilutions ( $\phi_v^0$ ) have usually been considered as the mean of the observed  $\phi_v$  values, whereas in the later cases these were determined by extrapolating  $\phi_v$  values to zero concentration of the polyelectrolyte. 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>165,166</sup>

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>159-162,167-169</sup> Empirical procedures have been developed to calculate and predict the partial molar volumes for non-ionic and ionic organic compounds in aqueous solutions.<sup>170,171</sup> However, the evaluation of the 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.

### **Present Investigation**

From the above discussion, it is apparent that the problem of polyion-polyion and polyion-counterion interactions is challenging as well as interesting. It is, therefore, desirable to explore this aspect using different experimental techniques to arrive at a definite conclusion. 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 operative in these solutions. In the present investigation, we have, therefore, utilized conductometry, viscosimetry and volumetry to study the solution behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media.

Sodium carboxymethylcellulose is a chemically modified cellulose derivative (Fig. 4) 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

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 methanol-water has been used. Methanol-water solutions are among the most extensively studied of all solvent mixtures.<sup>100,107,165-175</sup> These mixed solvents are of interest because the two solvents are fully miscible at room temperature and its

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neighbourhood and the relative permittivities of the mixed solvent media could be varied over a wide range.

It would, therefore, be interesting to investigate the behaviour of a polyelectrolyte both in absence and in presence of added electrolyte in these mixed solvents.

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## Chapter 2: Introduction

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