

## Chapter II

### Introduction

Systems containing polyelectrolytes and/or surfactants have been the subject of extensive investigation aimed at a fundamental understanding of their properties as well as evaluation of their use in various technical applications. In what follows we will highlight some of the important applications of different experimental techniques to polyelectrolyte solutions with particular reference to various aspects of some the transport and thermodynamic properties of polyelectrolyte solutions followed by a brief account of the polyelectrolyte-surfactant interactions as the present dissertation is concerned with some transport and thermodynamic studies on polyelectrolyte solutions and also with studies on the influence of polyelectrolyte on the aggregation behaviour of surfactant in solutions. Before discussing these aspects, a brief description of the polyelectrolytes and surfactants will be given.

#### **Polyelectrolytes**

##### *Definition of Polyelectrolytes*

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

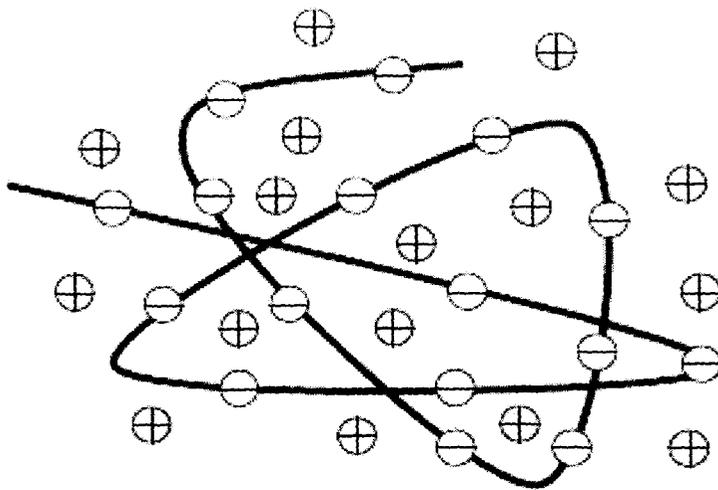
macromolecules. The behaviour of polyelectrolytes is also governed by such factors as the solution pH, nature of the ions, molecular weight, solvent polarity, temperature etc. Moreover the presence of the multivalent counterions significantly influences the structure and dynamics of the polyelectrolyte solutions.

### ***Classification of Polyelectrolytes***

There are different ways of classification of polyelectrolytes. It is possible to distinguish between natural, synthetic and chemically modified natural polyelectrolytes. Examples are DNA, sodium polystyrenesulfonate and carboxymethylcellulose, respectively. Polyelectrolytes may be grouped into linear, branched and cross-linked chains or into homo and copolymers. A polyelectrolyte could be a polyacid, a polybase or a polyampholyte depending upon whether the ionizable groups are all anionic, cationic or a mixture of both. Another distinction is also possible between strong polyelectrolytes, which acquire spontaneously full charge, and weak polyelectrolytes which are only partially charged upon dissolution.

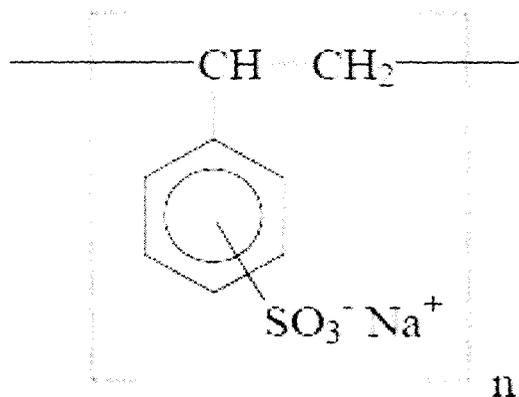
Based upon the molecular architecture, polyelectrolytes have been divided into two important categories, namely linear and branched polyelectrolytes. In linear polyelectrolytes, a large number of atoms are connected together to form the backbone chain. Although in a topological sense the backbone is 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 [Figures 1a and 1b] bear a macroion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions. Since both of these interactions occur almost simultaneously, it is rather difficult to study these systems. Sodium polystyrenesulfonate is an example of a flexible polyelectrolyte [Figure 1b]. Rigid rod-like



**Figure 1a.** Schematic representation of a flexible polyelectrolyte.

polyelectrolytes (Figures 2a and 2b) on the other hand, bear a macroion which does not undergo any conformational change due to steric constraints on such systems. Only the

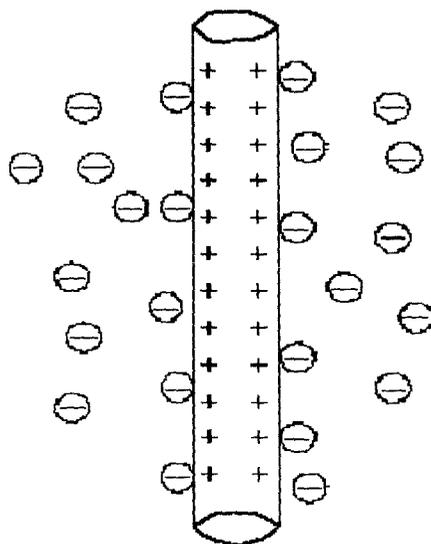


**Figure 1b.** An example of a flexible polyelectrolyte: sulphonated polystyrene with sodium counterions.

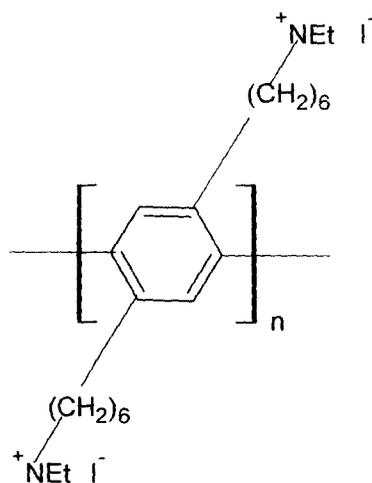
intermolecular Coulombic interactions determine the solution properties of these polyelectrolytes. An example of this type of polyelectrolyte is poly (*p*-phenylene) with iodine counterions (Figure 2b). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as, DNA, RNA and the tobacco-mosaic virus.

## Importance of Polyelectrolytes

Polyelectrolytes play an important role in molecular biology and materials science. For example, the natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building block of life, the nucleic acids and proteins are polyelectrolytes. These biopolymers play a central role in maintaining and propagating life in the simplest as well as complex biological systems. Research in the area of the binding of proteins and nucleic acids, enzymes and other biological components is important to understand the mechanisms of reactions occurring in biological systems.



**Figure 2a.** Schematic representation of a rigid rod-like polyelectrolyte.



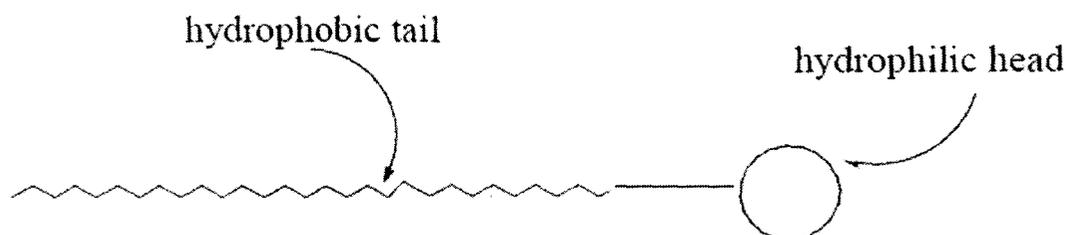
**Figure 2b.** An example of a rigid rod-like polyelectrolyte: poly (*p*-phenylene) with iodine counterions.

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

## Surfactants

### *Definition of Surfactants*

Surfactants are characterised by the presence of two moieties in the same molecule, one polar (known as hydrophilic in aqueous solution) and the other non-polar (hydrophobic) [Figure 3].



**Figure 3.** Structure of a surfactant molecule.

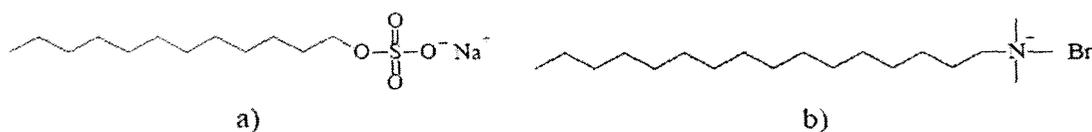
The behaviour of surfactants in aqueous solutions is determined by their tendency to move their hydrophobic part away from the solution and their hydrophilic part towards the solution. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates commonly known as micelles. In dilute solutions, surfactant molecules exist as individual species in the media and the solutions have completely ideal chemical and physical properties. As the surfactant concentration increases, chemical and physical properties of the solutions deviate from ideality by varying degrees, and at a certain concentration, aggregation of the surfactant monomers occurs and micelles are formed. This

concentration is called the critical micellar concentration (*cmc*). The critical micellar concentration indicates usually a narrow range of concentrations separating the limits below which most of the surfactant molecules is in the monomeric state and above which virtually all additional surfactant molecules enter the micellar state. The *cmc* is a very important solution property of surfactants. Presence of polyelectrolytes greatly influences the aggregation behaviour of surfactants through polyelectrolyte-surfactant interactions (discussed later).

### ***Classification of Surfactans***

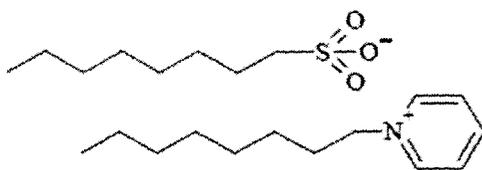
Surfactants can be classified according to their physical properties or functionalities. The following is the most common classification based on the nature of the head group.

The head group of an ionic surfactant can be ionized in an aqueous solution (*cf.* Figure 4). Depending on the outcome of this, there are a number of subcategories. If the charge on the head group is negative, the surfactant is said to be anionic. Among these, we find alkyl sulfates, alkyl sulphonates alkyl phosphates and fatty acid salts. If the residual charge is positive, the surfactant is cationic and common examples of this kind are alkyltrimethylammonium and alkylpyridinium halides.



**Figure 4.** Molecular structure of two common ionic surfactants: a) sodium dodecyl sulfate (SDS), and b) hexadecyltrimethylammonium bromide (CTAB)

In some ionic surfactant molecules the ionization leads to two separate groups of opposite charges attached to the hydrophobic part. Such surfactants are called zwitterionic and these are common in biological systems. This type of surfactant can also be regarded as nonionic, since their total charge is zero. Catanionic surfactants (Figure 5) consist of oppositely charged surfactant ions, *i.e.*, one surfactant acts as counterion to the other. Catanionic surfactants can be either symmetric (both alkyl chains are of the equal length) or asymmetric (one chain is shorter than the other).

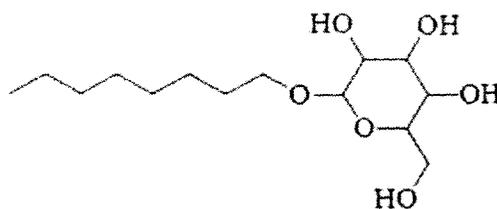


**Figure 5.** A symmetric catanionic surfactant, octylpyridinium octanesulphonate (OPOS).

The nonionic surfactants lack groups that can easily be ionized. Examples of nonionic surfactants with a polyoxyethylene and a polyhydroxy moiety are shown below (Figure 6). Compared to ionic surfactants of comparable size, nonionic surfactants form aggregates at lower concentration and the aggregation behaviour is less sensitive to the added salt due to the absence of repelling charges in the head groups.



a)



b)

**Figure 6.** Nonionic surfactants: a) pentaoxyethylene dodecyl ether ( $C_{12}E_5$ ) b) *n*-octyl  $\beta$ -D-glucoside (OG).

### ***Importance of Surfactants***

Surfactant solutions have unique properties, such as micelle formation due to hydrophobic interactions in aqueous solutions, counterion binding due to the high surface charge density of micelles, and the solubilisation of water-insoluble materials due to the formation of a hydrophobic domain. These properties make them extremely useful in their

widespread applications in diverse areas. Surfactants are essential for the formation of cell membranes, for the movements of nutrients and other important components through the membranes, for the suspension and transport of materials in the blood and other fluids, for respiration and the transfer of gases between the atmosphere (the lungs, for human being) and the blood, and for many other important biological processes. The primary traditional application of surfactants is their use as soaps and detergents for a wide variety of cleaning processes. These also find applications in cosmetics, and personal care products. Surfactants are an important part in the manufacture of leathers and furs. These are required in many capacities in the production of paints and lacquers, and in related coating systems. Surfactants are critical components in agricultural formulations for the control of weeds, insects, and other pests in agricultural operations. These species also play important roles in food-related industries, in chemical industries as phase transfer catalysts, in the preparation of polymer systems such as emulsion or latex polymer for textile manufactures, in pharmaceutical industries, in medical and biochemical research, in the manufacture of electronic microcircuits, and in new display and printing technologies, technologies, magnetic and storage media, and many more.

## **Behaviour of Polyelectrolytes in Solutions**

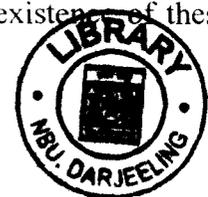
### ***Concentration Regimes in Polyelectrolyte Solutions***

The different properties of polyelectrolytes in solutions are very much dependent upon their concentrations in solutions. The three different concentration regimes in polyelectrolyte solutions, namely dilute, semidilute and concentrated regions, could be understood from the concept of overlap concentration which is defined as the concentration at which the polymer chains start to interact with each other *i.e.*, start to overlap. It is generally expressed as  $c^*$ . A dilute polymer solution, on the other hand, refers to the concentration region where the polymer chains are isolated and do not interact with the other chains. Here the polymer concentration is less than the overlap concentration,  $c^*$ . In dilute solutions, polyelectrolytes have a large overall size and a rather stiff local conformation.<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  $g_c$  monomers, bears a charge of  $q_D = z_c f e g_c$ , 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 bears an electric charge of  $q_\xi = z_c f e g$ . Because of the strong electrostatic interactions within each correlation blob, the chain is fully extended conformation of electrostatic blobs in the semidilute-unentangled regime ( $c^* < c < c_e$ ). At higher concentrations where  $c > c_e$ , significant overlap of neighbouring chains occurs, and this strongly affects the chain motion (semidilute-entangled regime). At even higher concentrations, the electrostatic blobs begin to overlap, and owing to the increase of electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments<sup>15</sup> suggest a polyelectrolyte behaviour similar to that of a neutral solution. Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration  $c^*$ , at which the distance between chains equals their extended length, a concentration  $c_e$  where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length (*i.e.*, Zimm-like dynamics up to the correlation length  $\xi_0$  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 nonequilibrium properties, such as viscosity, conductance, or diffusion. Experiments below the overlap concentration  $c^*$  are difficult to perform because of the very low concentrations and subsequently very low effects to be monitored, requiring extreme experimental sensitivity. Measurements above  $c_D$  also might be problematic, arising from the high solution viscosity. It is, therefore, not surprising that most of the experimental results described in the literature seem limited to the concentration region between  $c^*$  and  $c_D$ . The final conclusions as to the existence of these

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

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

In spite of the increasing theoretical and experimental efforts over the last 7-8 decades, the solution properties of polyelectrolytes are not yet completely understood. Extensive reviews and entire books have been devoted to the properties of polyelectrolyte 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 these subjects.

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 the counterion binding as an important concept in understanding the characteristic physicochemical properties of polyelectrolytes, *e.g.*, counterion activity and the dissociation constant.

Since the outset of polyelectrolyte research, electrochemical methods have been used as powerful tools to investigate and analyze the equilibrium properties as well as the transport phenomena.<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 the size and shape, both modified by interaction with the third component, for

example the salt, which influences the conformation of the macroion. Besides the scattering methods (discussed later), viscometry offers the possibility of studying conformational changes of polyelectrolytes, in particular, the influence of the ionic strength on the molecular dimension (please see later).

Viscosity is clearly a property of the solution as a whole under the influence of a mechanical perturbation. Diffusion phenomena, on the other hand, are directly related to the relative motion of solute particles in a stationary system. Various kinds of isothermal diffusion may be distinguished, which refer to different motions and are observed under different experimental conditions. For instance, the random motion of particles in a homogeneous system at thermodynamic equilibrium is responsible for density or concentration fluctuations. These motions are investigated by dynamic light scattering. On the other hand, diffusional fluxes arise in systems in which macroscopic chemical potential gradients exist for one or several thermodynamic species. An intermediate situation corresponds to the setup for self-diffusion measurement with fluxes of labelled molecules in a system containing a chemically identical species of different isotopic composition. All kinds of different diffusion measurements have been performed on polyelectrolyte solutions.<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 the varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.<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

the characterization of the molecular parameters of polyelectrolytes in solution.<sup>32,58-61</sup> For the past four decades there has been an increasing interest in dynamic scattering methods, particularly dynamic light scattering (DLS), because these could provide important insight into the dynamics of polyelectrolyte solutions to very high concentration, and these are also capable of providing useful structural informations, *e.g.*, translational diffusion coefficient and solvodynamic radius of the scattering species.

In particular, the main interest of light scattering studies on polyelectrolyte solutions was focused up to about 1980 on the investigation of coil expansion and the second virial coefficient in relation to the ionic strength of the medium, besides their function as routine method in determining the mass average molecular mass.<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 can be stated that the experimental data obtained from different scattering methods as to the intermolecular structure factor of semidilute salt-free polyelectrolyte solutions are qualitatively in good agreement, but quantitative discrepancies occur and the real structure models are not clear at present. Comprehensive and sophisticated experiments are necessary to prove the theoretical models in more details. A brief and very useful review on the application of these different scattering techniques is available in Dautzenberg *et. al.*<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, hence, could provide important information on the interactions between the polyions and the counterions and also on the conformation of the polyions in solution.

Here, we shall particularly dwell upon different aspects of transport and thermodynamic properties of polyelectrolytes, as the present dissertation is intimately related to the studies of electrical conductances, viscosities, and partial molar volumes of sodium polystyrenesulfonate (NaPSS), containing both hydrophobic phenyl moiety and hydrophilic sulfonate group, in acetonitrile-water mixed solvent media. The effects of added salt will also be considered.

## **Polyelectrolyte Conductance**

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

The specific conductance and the equivalent conductivity,  $\Lambda$ , are experimentally determined parameters which are suitable to describe the electrolytic transport properties of polyelectrolyte solutions because these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field. The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory<sup>19,94-98</sup> for dilute solutions. This theory relies on the following ideas:

- (1) The real polyelectrolyte chain can be replaced by an infinite line charge.
- (2) Interactions between two or more polyions are negligibly small.
- (3) The relative permittivity ( $D$ ) in the condensation volume of the polyelectrolyte is that of the pure solvent.
- (4) The central parameter of the theory is the linear charge density parameter ( $\xi$ ) 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 on to the polyion to yield the critical value  $\xi = 1$ . If, on the other hand,  $\xi < 1$ , ionization takes place to reach this critical value.

- (5) The uncondensed mobile ions are treated by the Debye-Hückel approximation.

A limiting law of electrical 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  $z_c$

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

where the parameter  $a$  is the radius of the 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, which is defined by

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

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

### ***Limitation of the Manning Model***

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

A survey of the literature indicated that although in a limited concentration range, the change of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not generally agree

with the predictions. This aspect has been amply described in the reviews by Bordi *et. al.*<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 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  $1 \times 10^{-2}$  equiv L<sup>-1</sup> for all counterions and the two investigated polyelectrolytes of molar masses of 70,000 and 500,000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the increase after the minimum was passed could not be explained. It was concluded that the applicability of the Manning theory is questionable for a concentration range where chain coiling is probable. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonate in semidilute solutions were carried out by Szymczak *et. al.* at 298.15 K.<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 carrying different charge density parameters that, although qualitative agreement is obtained with the Manning limiting law, the concentration dependence predicted is in agreement with the experimental curves only for the polyions with a relatively low charge density. The behaviour of dextran sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rodlike structure on which the theory is based.

Significant deviations of the experimental equivalent conductivities of sodium and potassium dextran sulfate from the Manning predictions in the semidilute concentration regime were also reported by Beyer and Nordmeier.<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<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 4,000, 167,000 for both the dilute and semidilute regimes. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polymer molecular weight. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molecular weight sample is hardly surprising, since these data are all above  $c^*$ , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molecular weight sample is noteworthy since these data are all below  $c^*$ .

In a study on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-*co*-(vinyl pyrrolidone)], 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.

The failure of the Manning model to describe the electrical conductivity behaviour of solutions of sodium carboxymethylcellulose and sodium polystyrenesulfonate in aquo-organic mixed solvent media has also been reported.<sup>107-109</sup>

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

### ***Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions***<sup>110</sup>

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*<sup>110</sup> using the scaling description proposed by Dobrynin *et al.*<sup>111</sup> for the configuration of a polyelectrolyte chain.

In the semidilute solutions, the polyion chain is modeled 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  $\xi_0$ .

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

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

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

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

The equivalent conductance of the polyelectrolyte solution is then given by

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

The above expression given by Colby *et al.*<sup>110</sup> is derived taking into account the scaling arguments proposed by Dobrynin *et al.*<sup>111</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  $A$ , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge-density parameter  $\xi = \lambda_B / b$ , Eq. (9) can be applied to more concentrated systems, up to the concentration  $c_D$ , where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This new model has been applied, so far, to a limited number of aqueous polyelectrolytes<sup>31,93,110,112</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>113</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>114</sup>

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

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

An approach which is usually used in the literature in describing the behaviour of salt-containing polyelectrolyte solutions is to analyse the experimental data phenomenologically in terms of an additivity contributions of the polyelectrolyte and the simple salt to the total specific conductivity.<sup>115-118</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,

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

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. In a polyelectrolyte-salt solution, therefore, the polyelectrolyte specific conductance is given by,

$$\kappa_p = \kappa - \kappa_s$$

If a true additivity holds, the values of  $\kappa_p$  obtained for a given polyelectrolyte in salt-free (where  $\kappa_s = 0$ ) and salt-containing solutions would be identical. However, this is not observed for different polyelectrolyte-salt combinations investigated earlier.<sup>115-118</sup> Thus the true value of the polyelectrolyte specific conductance cannot be calculated from conductance data obtained in salt-containing polyelectrolyte solutions by using additivity of polyelectrolyte and simple salt specific conductances indicating clearly the existence polyelectrolyte-salt interactions. The observed deviation may be attributed to the changed conformation of the polyion in presence of an added salt as a result of the interactions of salt with the polyelectrolyte compared to that present in the salt-free solutions. Changes in the specific conductance contribution of the counterions in presence of a salt may also contribute to the observed deviation.

Kowblansky and Ander,<sup>115</sup> therefore, modified the 'primitive' additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

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

where  $D_2$  and  $D_2^0$  are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients  $D_2 / D_2^0$  has been used as a quantitative measure of the effective interactions of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be  $\kappa_s(D_2 / D_2^0)$ .

Now, in absence of the experimental data for  $D_2 / D_2^0$  for the present system, these were calculated by using the Manning theory as,<sup>115</sup>

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

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

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

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

Although the modified additivity has been shown to offer some improvement over the primitive one, significant departures are also noticed in some cases.<sup>115-118</sup> Therefore, the effect of salts on the conductance is not described by the additivity even if the interactions among all species of ions in solution are taken into account through Eqs. (12) – (14).

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

conductance may be influenced by the solute-solvent solvodynamic interactions. Namely, the specific conductance depends on whether the polyion is free-draining or non-draining. It should be pointed out that the polyion mobility, however, has been understood not to be so sensitive to the ionic strength.<sup>67</sup> In addition, there is no direct evidence that the conformational change provides a drastic deviation from the additivity of conductance. Further studies on different polyelectrolyte-salt systems in various solvent media might be helpful in providing light on the interactions occurring in such systems.

## **Polyelectrolyte Viscosity**

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

Viscosity is an important tool for the determination of molecular structure and conformation of a polymer of either type neutral or charged. In case of neutral polymer solutions, the reduced viscosity  $\eta_{sp}/c$  (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 in the absence of polymer and  $c$  is the (monomer) concentration of the polymer solution) is proportional to  $c$ . This well-known relation 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 concentration dependence of viscosity. Early investigations of the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that reduced viscosity would increase without bound as one lowers the polyion concentration. In these studies, which are summarized in the pioneering work of Fuoss,<sup>119,120</sup> a straight line is obtained when the reduced viscosity is plotted as a function of the square root of the polymer concentration. It is usually assumed that this line could be extrapolated to zero concentration and that the intercept at zero concentration gives the intrinsic viscosity. However, careful investigation of the dilute solution behaviour revealed that the apparently unbounded increase of the reduced viscosity is always followed by a maximum,<sup>121-124</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>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 four

and a half decades, was generally interpreted as the result of expansion and shrinking of the flexible macroion due to short-range interactions. Most of these investigations were performed on weak polyelectrolyte systems *e.g.*, derivatives of polyvinylpyridine and polymers containing carboxylic acids, as reviewed by Tanford.<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) sodium salt<sup>130</sup> sodium polystyrenesulfonate,<sup>122,131</sup> sodium carboxymethylcellulose<sup>132</sup> polysulfobetaines,<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 characterised 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 interaction and of conformational change of the polyion on the 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,

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

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

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

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

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

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

Antonietti *et. al.*<sup>142,143</sup> expressed the reduced viscosity for charged latex particle as,

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

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. 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. Antonietti *et. al.*<sup>142</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 quantitative information, since each parameter value is rather unstable.

### ***Intrinsic Viscosity***

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

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

At a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity  $\eta_{sp}/c$  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>2,144</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.

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

The determination of the intrinsic viscosity is more straightforward if the isoionic dilution method<sup>124,145</sup> is applied. Following this method, a polyelectrolyte solution in the pure solvent (in absence of any low molar mass salt) is diluted with solutions of increasing concentration of a salt. The dilution of the solution is performed in such a way that after each addition, the total ionic strength of the solution remains the same and equal to the original value due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these conditions the reduced viscosity decreases linearly as one lowers the

polyelectrolyte concentration and thus extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength. Moreover, since the ionic environment around the polyions remains unaffected as a result of isoionic dilution, the original conformation of the polyion under salt-free situation is assumed to be preserved.

In spite of the success of this method for the determination of intrinsic viscosity in a convenient manner, however, very little attention was paid to this direction so far.<sup>124,129,145,146</sup>

### Partial Molar Volumes of Polyelectrolytes

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

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

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 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>147-152</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>153,154</sup>

Various concepts concerning the electrostrictional hydration effect, the hydrophobic structural effect, and counterion-binding on to the polyion chain in polyelectrolyte solutions were interpreted on the basis of this property.<sup>147-150,155-157</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>158,159</sup> However, the evaluation of the partial molar volumes by these procedures is limited because of the lack of availability of reliable experimental data for a broad variety of polyelectrolyte species.<sup>151</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.

### **Interaction of Polyelectrolytes with Surfactants**

As discussed earlier the properties of polyelectrolyte solutions are extremely sensitive to their environment. The effect is ascribed to the coiling of the initially highly extended macroion chain due to the shielding of polyelectrolyte charges by the simple electrolyte. Another interesting problem is related to the changes of chain conformation arising from the binding of surfactant ions.

Interactions between a polyelectrolyte and surfactant in aqueous solutions have been investigated for several decades and are extensively documented.<sup>160-164</sup> In particular, there have been significant research efforts focusing on the interactions between polyelectrolytes and oppositely charged surfactants in recent years.<sup>164-182</sup> Indeed such studies can be applied to a large number of industrial as well as biological processes. The association between the polymers and surfactants has been largely rationalized as a consequence of hydrophobic and electrostatic interactions.<sup>183,184</sup> While interactions between non-ionic polymers and ionic surfactants rely mainly on hydrophobicity,<sup>161,185</sup> attractive electrostatic forces dominate in the case of polyelectrolytes and oppositely charged surfactants. In the presence of an oppositely charged polyelectrolyte, micelle-like aggregates start to form along the polymer chain surfactant concentration as the surfactant concentration exceeds a critical value referred to as the critical aggregation concentration (*cac*). The *cac* is thus an analog of the critical micellar concentration, *cmc* (the concentration above which micellar aggregates begin to form in a pure surfactant solution),<sup>186</sup> but in solutions of surfactants with added polymeric component. A characteristic feature of this parameter is that it is always lower than the *cmc* of the corresponding surfactant. The lower *cac* is particularly pronounced in solutions of polyelectrolytes with opposite charge to the surfactant. With the increase in the surfactant concentration, a second transition known as the polymer-saturation point (*psc*) is obtained.

Afterwards, the concentration of surfactant monomer builds up until free surfactant micelles start to form at a concentration commonly known as the apparent critical micellar concentration (*cmc*).

The experimental efforts in this field were first devoted to the determination of binding isotherms,<sup>163,173,187-189</sup> enthalpies of binding,<sup>170,190</sup> and various thermodynamic and transport properties<sup>181,191</sup> in solutions of polyelectrolytes with added surfactants. Different experimental techniques used to study polymer-surfactant interactions include conductometry, tensiometry, viscometry, calorimetry, turbidimetry, volumetry, Nuclear Magnetic Resonance (NMR) measurements, fluorescence, gel permeation chromatography (GPC), Fourier Transform Infrared (FTIR) spectroscopy, electromotive force (EMF) measurements, light scattering techniques e.g., DLS, SAXS, SANS etc.<sup>192,193</sup>

In this dissertation, we have employed conductometry and tensiometry to investigate the interactions between NaPSS and CTAB. These two are very powerful tools to study these interactions. Conductometry provides the *cmc* of a pure surfactant solution as the intersect of two straight lines in the pre- and postmicellar regimes of the specific conductivity ( $\kappa$ ) vs. surfactant concentration profile. In polyelectrolyte-surfactant systems, the conductometric patterns usually exhibit three linear regions, below the *cac*, between the *cac* and the *psc*, and above *psc* with two points of intersection, the former of which corresponds to the *cac* while the latter to *psc*.<sup>172,194</sup> More complex conductometric profiles, showing four linear sections (below the *cac*, between the *cac* and *psc*, between *psc* and *cmc\**, and above the *cmc\**) with gradually decreasing slopes with three breaks have also been reported.<sup>169,170</sup> It should, however, be pointed out that Kogej and Skerjanc,<sup>181</sup> were able to identify two linear sections in the polyelectrolyte-surfactant specific conductivity ( $\kappa$ ) vs. surfactant concentration profiles and hence were only able to determine the *cmc\**. However, they were successful in detecting the formation of polyelectrolyte-induced surfactant aggregates above *cac* from the plots of the molar conductivity ( $\kappa$ ) versus the square root of the surfactant concentration.

The tensiometry has been an elegant method for the understanding of polymer-surfactant interactions. In tensiometric determination of the *cmc* of pure surfactants, the surface tensions ( $\gamma$ ) are plotted as a function of logarithm of the surfactant concentration and the *cmc* is realized as the surfactant concentration where the profile reaches a plateau. The  $\gamma$  - log[surfactant] curves for polyelectrolyte-surfactants, on the other hand, are not so simple. It was Jones<sup>195</sup> who studied the properties of mixed poly(ethylene oxide) (PEO)/sodium

dedecylsulfate (SDS) systems and first formalized the concept, in a system of fixed polymer concentration and increasing amounts of surfactant, using two critical concentrations of the surfactants. When an increasing amount of surfactant is added, the concentration of surfactant on the water/air interface increases. This is manifested as a reduction in surface tension in the beginning until the concentration at which the cooperative interaction between the surfactant and the polymer first occurs indicating the onset of micelle formation on the polymer. The surface concentration of the surfactant does not increase, because all added surfactant associates with the polymer. This results in a flat part in the surface tension-log[surfactant] curve. This invariance of surface tension with log[surfactant] then terminates at a surfactant concentration at which the polymer becomes saturated by the surfactant and the surface tension starts to decrease again. A concentration of surfactant is finally reached beyond which addition of surfactant can hardly affect the surface tension of the solution. This inflection marks the surfactant concentration where all added surfactant start to form surfactant micelles. Though this type of tensiometric profiles are rather common, a slight difference in the variation of surface tension as a function log[surfactant] was reported by Prasad *et. al.*<sup>169</sup> for polyvinylpyrrolidone (PVP)-SDS interaction. These authors identified the first minimum in the tensiometric profile as the *cac*. In this study, small aggregates start forming by the interaction of SDS with the polymer. Two processes, (1) binding of small SDS aggregates with PVP in the bulk and (2) binding of aggregates with PVP at the interface then occurred. The first process did not effect  $\gamma$ , whereas the second dislodged the polyelectrolyte to sink into the bulk from the interface; consequently, the interface was stripped off both from PVP and SDS with an increase in  $\gamma$  until the binding process was complete manifested as a maximum in the tensiometric profiles; this concentration where the binding process was complete is considered as the polymer saturation concentration (*psc*). Upon completion of the process, there was monomer buildup at the interface associated with a decline in  $\gamma$  until free micelles started to form in solution beyond which addition of CTAB can hardly affect the surface tension of the solution. The onset of this plateau in the surface tension curve corresponds to the critical micellization concentration for the formation of pure surfactant micelles in presence of the polyelectrolyte; this concentration is, generally, referred to as the apparent critical micellization concentration (*cmc\**). Park *et. al.*<sup>196</sup> observed a similar behaviour of the tensiograms for the interactions of anionic polyelectrolytes with cationic surfactants. Careful analyses of the tensiograms provide useful information on the

characteristic concentrations mentioned above – a detailed account of which is given in Chapter IX with reference to NaPSS-CTAB interaction.

From a survey of the literature, it is apparent that various concepts concerning the polymer-induced surfactant aggregation, formation of polymer-surfactant complexes, wrapping of these aggregates by the polymer chain and coiling/decoiling of the polyion chain in presence of surfactants in polymer-surfactant solutions were interpreted on the basis of these studies.

### **Present Investigation**

From the above discussion, it is apparent that the problem of intrapolyion, polyion-counterion and polyion-surfactant interactions is intriguing as well as interesting. It is, therefore, desirable to attack this problem 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 and polyelectrolyte-surfactant solutions from a more general point of view compared to those in aqueous solutions since use of a series of mixed solvents corresponds to a gradual change in the relative permittivity of the media and hence in the interactions prevailing in these solutions. We have, therefore, utilised three important methods *viz.*, conductometry, viscometry, and volumetry to study the behaviour of NaPSS. On the other hand we have, utilized two important methods conductometry and tensiometry to study the interaction between NaPSS-CTAB in acetonitrile-water mixed solvent media.

NaPSS is a synthetic polyelectrolyte. The polyion is readily soluble in water, and is insoluble in lower alcohols. It may be prepared by polymerization or copolymerization of sodium styrenesulfonate or by sulfonation of polystyrene. NaPSS contains both hydrophobic phenyl moiety and hydrophilic sulfonate group. NaPSS is used as a superplasticizer in cement, as a dye improving agent for cotton and as proton exchange membranes in fuel cell applications. Crosslinked polystyrenes that are then sulfonated have found widespread use in ion-exchange applications. This polyelectrolyte (Kayexalate, Kionex) is a medication used to treat abnormally high potassium levels.<sup>197</sup> This ionic polymer can interact with the most commonly used cationic surfactant CTAB by hydrophobic as well as electrostatic forces. This resembles the interaction of many biological macromolecules.

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. On the other hand the main factors that govern in the case of oppositely charged polyelectrolyte and surfactants solutions are firstly, strong interactions are observed due to a contribution of electrostatic forces and cooperative hydrophobic effects between bound surfactant ions. The difference in behaviour has been explained by inclusion of the hydrophobic aromatic group on PSS into the surfactant minimicelle leading to formation of a very stable aggregate. This is accompanied by a release of considerable amount of counterion of the polyelectrolytes and surfactants into the solution. Both of these factors are related to the relative permittivity of the solvent media. Use of a series of mixed solvents corresponds to the systematic change in the relative permittivity of the media. In this study, the mixed solvent acetonitrile-water has been used. Acetonitrile-water solutions are among the most extensively studied of all solvent mixtures.<sup>198-205</sup> These mixed solvents are of interest because although the two solvents are fully miscible at room temperature, the components have very different chemical natures. The relative permittivities of the mixed solvent media could be varied over a wide range. In addition, acetonitrile-water mixtures are of considerable technological interest, *e.g.* for the recovery of precious metals from concentrates<sup>205,206</sup> and for the removal of iron from hydrometallurgical leach liquors.<sup>207</sup> Extensive thermodynamic and other physical measurements have been made on acetonitrile-water mixed solvent media both in the presence and absence of dissolved electrolyte.<sup>198-205,208</sup> It would be, therefore, interesting to investigate the behaviour of a polyelectrolyte in these mixed solvents.

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