

Chapter II

Introduction

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

Electrostatic interactions play a very important role in determining the properties of these systems. Since 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 with oppositely charged surfactants can be studied from a more general point of view in mixed solvent media. Unfortunately, studies on polyelectrolyte-surfactant interactions in mixed solvent media are completely absent.

For a better understanding of the interactions between polyelectrolytes and oppositely charged surfactants, a comprehensive investigation on the polyelectrolyte-surfactant interactions in mixed solvent media is therefore, essential. An understanding of the behaviour of polyelectrolytes in these mixed solvent media is, of course, a prerequisite for this purpose.

The aim of this thesis is, therefore, to elucidate (a) the behaviour of a selected polyelectrolyte and (b) the nature of its interactions with an oppositely charged surfactant 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 followed by an account of the polyelectrolyte-surfactant 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 macromolecular compound containing a large number of ionizable or ionic groups which are soluble in a suitable polar solvent (generally water). Technically speaking, polymers which undergo ionization in solution are referred to as polyelectrolytes. Some common examples of the polyelectrolytes include proteins, nucleic acids, carrageenans, pectins, xanthan gum, polyacrylic acid and

polystyrenesulfonate. Under appropriate conditions in solution, the ionizable groups of polyelectrolyte molecules dissociate into 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 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 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

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

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 polymer might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.¹ Branched polyelectrolytes do not have linear chains and are less investigated species compared to their linear analogues.²⁻⁷ The different known branched

structures are comb-like, stars (regular and irregular), H-shaped, super H-shaped polymer and dendrimers.^{3,8-13}

Polyelectrolytes could also be distinguished depending upon their conformations. Flexible polyelectrolytes (Figures 1 and 2) consist of 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 2). Rigid rod-like

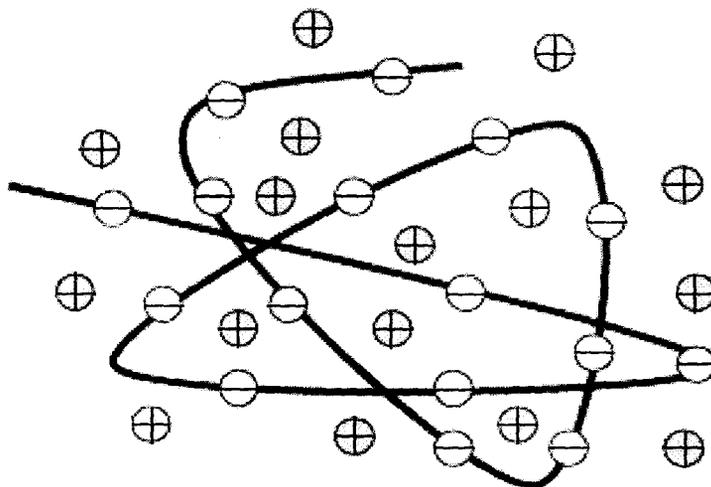


Figure 1. Schematic representation of a flexible polyelectrolyte.

polyelectrolytes (Figures 3 and 4) on the other hand, contains a macroion which does not undergo any conformational change due to steric constraints on such systems. Only the

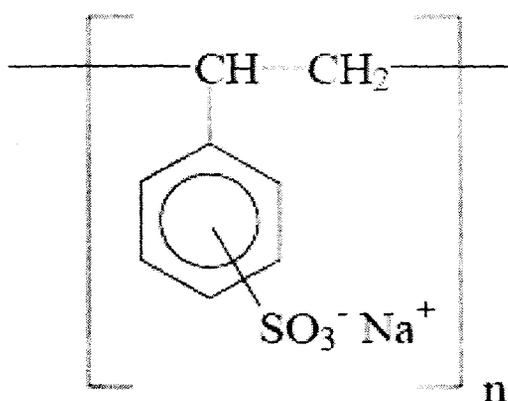


Figure 2. An example of a flexible polyelectrolyte: sulphonated polystyrene with sodium counterions.

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 4). 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 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.

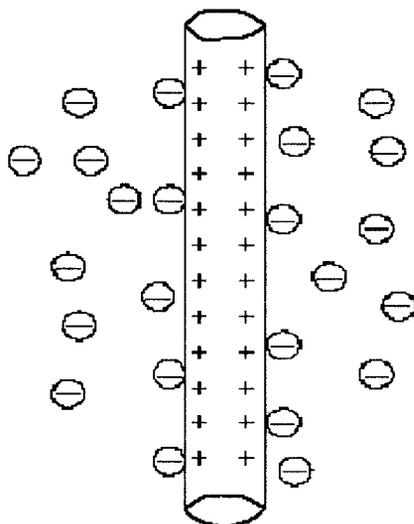


Figure 3. Schematic representation of a rigid rod-like polyelectrolyte.

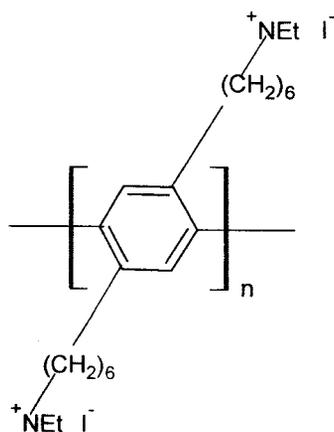


Figure 4. An example of a rigid rod-like polyelectrolyte: poly (*p*-phenylene) with iodine counterions.

Synthetic polyelectrolytes have been a very active area of scientific research and commercial growth. Conformations of the polyelectrolytes as well as the interactions 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.¹⁴⁻¹⁸ Potential applications in medicine and biomedical engineering are also being extensively pursued.

Surfactants

Definition of Surfactants

Surfactant molecules, in general, consist of two different kinds of moieties namely, a polar part (known as the hydrophilic part in aqueous solution) and a nonpolar (hydrophobic) part (Figure 5).

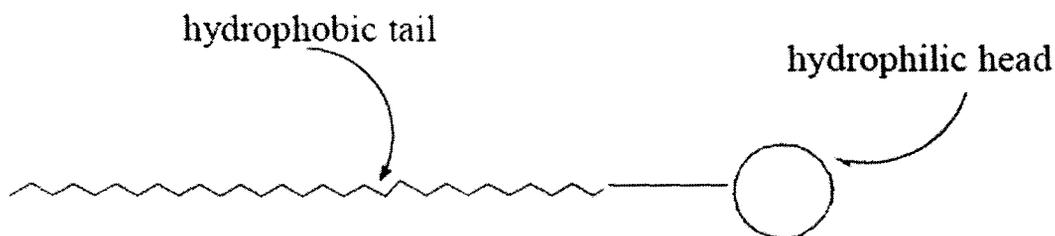


Figure 5. General structure of a surfactant molecule.

The behaviour of surfactants in aqueous solutions is determined by their tendency to direct their hydrophilic part towards the solution and their hydrophobic part away from the solution. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of aggregates commonly known as micelles (Figure 5a).

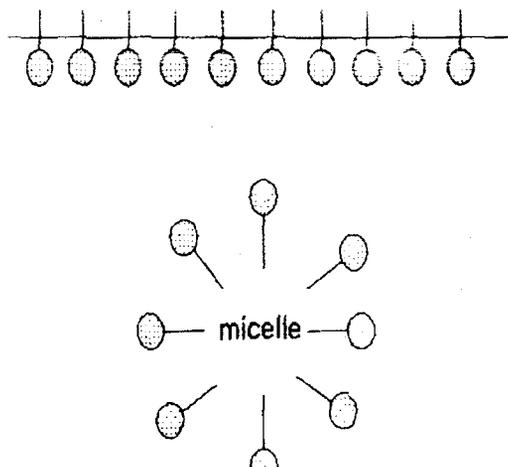


Figure 5a. Schematic representation of surfactant molecules at surface and surfactant micelle in bulk liquid.

Micelles consist of hydrophobic interior regions, where hydrophobic tails interact with one another. These hydrophobic regions are surrounded by the hydrophilic regions where the heads of the surfactant molecules interact with water. At very low concentration in water, surfactant molecules are unassociated. Above a certain concentration, the so-called critical micellar concentration (*cmc*), almost all of the added surfactant molecules are consumed in micelle formation, and the monomer concentration does not increase as the concentration is increased. The critical micellar concentration indicates usually a narrow range of concentration 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 affects the aggregation behaviour of surfactants through polyelectrolyte-surfactant interactions.

Classification of Surfactants

Surfactants can be classified in accordance with 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 ionizes in aqueous solutions (*cf.* Figure 6). If the charge on the head group is negative, the surfactant is said to be anionic. For example, alkyl sulfates, alkyl sulphonates, alkyl phosphates and fatty acid salts are anionic surfactants. If, on the other hand, the head group charge is positive, the surfactant is cationic and common examples of this kind are alkyltrimethylammonium and alkylpyridinium halides.

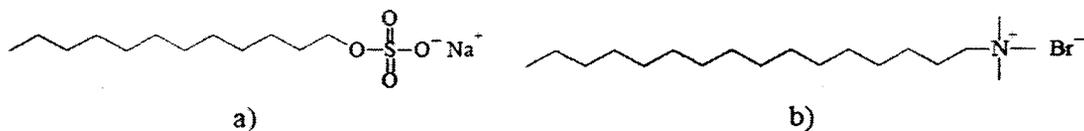


Figure 6. Molecular structure of two common ionic surfactants: a) sodium dodecyl sulfate (SDS), and b) hexadecyltrimethylammonium bromide (CTAB).

In some ionic surfactant molecules, ionization gives rise to two separate groups of opposite charges attached to the hydrophobic part. Such surfactants are called zwitterionic and are common in biological systems. These can also be regarded as nonionic, since their overall charge is zero. Catanionic surfactants (Figure 7) consist of oppositely charged surfactant ions, *i.e.*, one surfactant ion acts as the counterion of the other. Catanionic surfactants can be either symmetric (both alkyl chains are of the equal length) or asymmetric (dissimilar chain length).

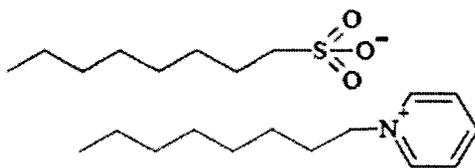


Figure 7. A symmetric catanionic surfactant, octylpyridinium octanesulphonate (OPOS).

Nonionic surfactants are characterized by the presence of groups that can easily be ionised. Examples of nonionic surfactants with a polyoxyethylene and a polyhydroxy moiety are shown below (Figure 8). Compared to ionic surfactants of comparable size, nonionic surfactants form aggregates at lower concentration and their aggregation behaviour is less sensitive to the added salt due to the absence of repelling charges in the head groups.

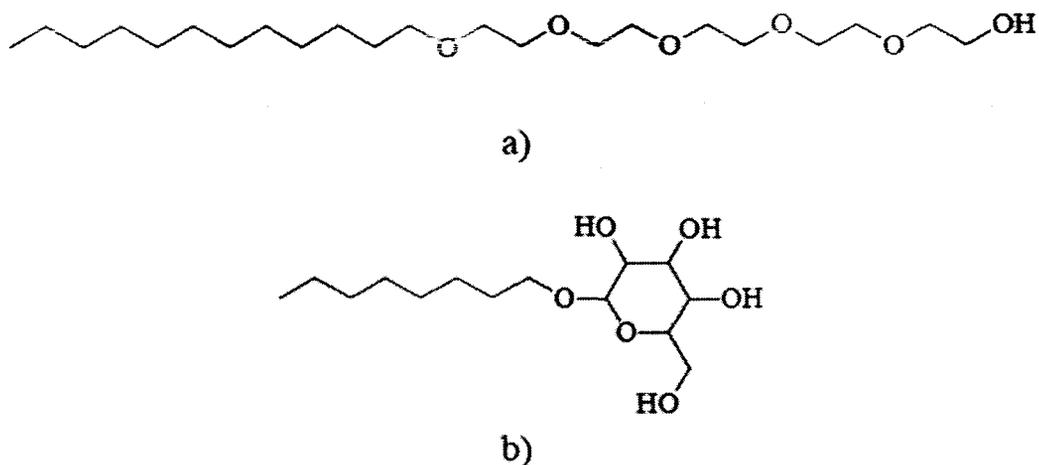


Figure 8. Nonionic surfactants: a) pentaoxyethylene dodecyl ether (C₁₂E₅) b) *n*-octyl β-D-glucoside (OG).

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 solubilization of water-insoluble materials due to the formation of a hydrophobic domain. These properties make them extremely useful in their versatile 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 important 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, magnetic and storage media, and many more.

Behaviour of Polyelectrolytes in Solutions

Concentration Regimes in Polyelectrolyte Solutions

The properties of polyelectrolytes in solution are very much dependent 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 the neighbouring chains. In such solutions, polyelectrolytes have a large overall size and a rather rigid local conformation.¹⁹ The chain is represented by an extended rod-like configuration of N_D electrostatic blobs of size D in the dilute regime. Each of them, with g_e monomers, bears a charge of $q_D = z_c f e g_e$, with z_c being the counterion valence, e the electronic charge, and f the fraction of ionized charged groups on the polyion chain (*i.e.*, the fraction of uncondensed counterions). As the polyelectrolyte concentration increases, the 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_ξ correlation blobs of size ξ_0 , each containing g monomers in semidilute solutions. Each blob bears 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 arguments²⁰ suggest a polyelectrolyte behaviour similar to that of a neutral polymer solution. Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration c^* , at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the

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correlation length (*i.e.*, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the strand of N/g beads of size ξ_0). In short, a polyelectrolyte solution 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 $c < c^*$. In so far 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.²¹ 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^* . The final conclusions as to the existence of these and other possible concentration regimes, if any, require more extensive experimental investigations and further theoretical efforts.

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 not yet completely understood. There are extensive reviews and entire books on the properties of polyelectrolyte solutions²¹⁻³⁷ and no attempt will, therefore, be made here to provide a comprehensive review of the vast literature which exists on these subjects.

Although early studies on synthetic polyelectrolytes have been reported in the 1930s,³⁸⁻⁴⁵ the beginning of systematic studies is dated back to the mid-1940s, when a study was initiated by Katchalsky at the Weizmann Institute, Israel⁴⁶ 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, Kagawa⁴⁷ 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^{21,29,36,48} of polyelectrolytes. The progress in the development of sophisticated equipments in conjunction with the availability 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.^{21,24,29,30,36,48} 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.^{2,36}

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, referring 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. 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.² 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.^{2,21}

In principle, sedimentation measurements should provide information on the properties of salt-free polyelectrolyte solutions, but no appropriate theoretical approaches and experimental investigations are available at present, which allows the use of sedimentation measurements in this respect.⁴⁹ However, at sufficiently high amounts of supporting low molar mass electrolytes, the motion of the polyions and the counterions is largely decoupled and ultracentrifugation is a powerful tool for molecular mass determination. Additionally, the conformational changes of the polyions with varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.^{2,50,51}

In separation and analysis of biopolymers, especially proteins, gel electrophoresis has been a well-established and successful tool for a long time. But studies on the gel electrophoresis for synthetic polyelectrolytes are relatively scarce.^{2,24} 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.^{2,52-55}

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.² These properties have been widely 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,^{2,21,56-61} information on the osmotic coefficients and the Donnan equilibria of polyelectrolytes are 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^{60,61} and the results indicated failure of the Manning and the Poisson-Boltzmann cell models. Afterwards, an analysis performed by Deserno *et al.*⁶² 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 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. The dielectric methods are still one of the most important techniques for studies on the structure and dynamics of polymer solutions in spite of their establishment well over a century. This is because of the fact that the relaxation processes occurring in aqueous polymer solutions in an extremely wide range of characteristic times, approximately from 10^{-12} through 10^3 s can be investigated by these methods. Information about 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.³⁶

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.^{37,63-66} 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 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 with respect to the ionic strength of the medium, besides their function as routine method in determining the mass average molecular mass.⁶⁷⁻⁷¹ 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 very low added-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.^{69,72,73} 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.⁷⁴⁻⁷⁷ For unfolded proteins, the chain statistics may be checked by SAXS in combination 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.^{78,79}

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.⁷⁵⁻⁸⁷

Despite the variety of conformational effects that may be studied by DLS in salt-containing polyelectrolyte solutions, large number of studies have been devoted to fundamental problems of the structures of polyelectrolyte solutions at low ionic strength, and their dependence on polymer concentration, ionic strength, and molecular mass.^{2,88-90}

It can be stated that 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 not clear at present. To prove 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.*²

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 counterions⁹¹⁻¹⁰⁵ 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 information on 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 particularly dwell upon different aspects of transport and thermodynamic properties of polyelectrolytes relevant to the present dissertation. This will be followed by a discussion on the interactions between polyelectrolytes and surfactants.

Some Important Properties of Polyelectrolyte Solutions

Polyelectrolyte Conductance

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

Manning Model for the Conductance of Salt-Free Polyelectrolyte Solutions

The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory^{24,106-110} for dilute solutions based on counterion condensation for an infinitely long and thin line charged chain. The basic idea is that if the charge density of the rod exceeds a critical value, some charges on the chain can be partially neutralized by the free ions in the solution, which means that the repulsive Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy $k_B T$.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by^{24,108,110}

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

where e is the protonic charge, D the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzmann constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense onto the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law for the electrical conductivity for a salt-free polyelectrolyte solution is related to ξ by the following equation^{107,108}

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

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and the parameter f is given by^{24,108,110}

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

In contrast to Huizenga¹¹¹ 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 the electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolytes,¹⁰⁹ and it follows for counterions with a charge of z_c

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

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

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

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

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

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

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 within 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.*³⁶ and Wandrey and Hunkeler⁴⁸ 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 presented¹⁰⁸ 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 Hayes¹¹² and Szymczak *et al.*¹¹³ 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 Hayes¹¹² studied the electrical conductances of lithium, sodium, potassium, cesium, magnesium, calcium, and strontium salts of polystyrenesulfonic acid covering the dilute and semidilute regimes (*i.e.*, above and below the overlap concentration, c^*) at 298.15 K. They observed a minimum in the equivalent conductivity in the range 7×10^{-3} to 1×10^{-2} monomol.L⁻¹ for all counterions and for 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 the 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.¹¹³ 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.*^{114,115} 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 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.¹¹⁶

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.⁹⁷

Wandrey¹¹⁷ 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.*⁹⁸ compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4,000 and 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)], Rios¹¹⁸ 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.⁹⁹⁻¹⁰¹

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

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*¹¹⁹ using the scaling description proposed by Dobrynin *et al.*¹²⁰ for the configuration of a polyelectrolyte chain.

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

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

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

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

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

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

The equivalent conductance of the polyelectrolyte solution is then given by

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

The above expression given by Colby *et al.*¹¹⁹ is derived taking into account the scaling arguments proposed by Dobrynin *et al.*¹²⁰ neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. As can be seen the above model has a single free parameter f , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge density parameter $\xi = \lambda_B / b$, 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^{36,98,119,121} 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.¹²² 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 methanol-water mixed solvent media.¹⁰³

Effect of Salts on the Conductance of Polyelectrolyte Solutions

Although the polyelectrolyte conductivities have been well understood in salt-free semidilute solutions¹¹⁹ in the light of the scaling description for the configuration of a polyion chain in accordance with Dobrynin *et al.*,¹²⁰ the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions. Devore and Manning¹²³ 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 theory¹²⁴ 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.¹²⁵⁻¹²⁹

Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

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

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_s is the specific conductance of the simple salt in the absence of polyelectrolyte.

However, earlier investigations¹²⁵⁻¹²⁹ suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, Eq.(10).

Later Ander *et al.*^{125,126} modified the “primitive” additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

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

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 measure¹²⁴ 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 $\kappa_s \left(D_2 / D_2^0 \right)$.

Although the “modified” additivity has been shown to be somewhat better than the “primitive” one, the departures from the experimental results are still prominent.¹²⁵⁻¹²⁹ Later, Bordi *et al.*¹³⁰ evaluated equivalent conductances for a hydrophilic polyion with a salt in the light of scaling theory approach¹²⁰ and compared them with their experimental results. The agreement is rather good, although a quantitative description is still awaiting.

Very recently, one of us has introduced¹⁰⁵ 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.¹¹⁹ This new model has been extensively tested with data on sodium polystyrenesulfonate in the presence of sodium chloride in 2-ethoxyethanol-

water mixed solvent media at different temperatures 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.*,¹¹⁹ the specific conductivity of a salt-free polyelectrolyte solution (c_p) neglecting the asymmetry field effect is given by

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

where λ_c^0 is the limiting equivalent conductivity of the counterions, c_p the number density of monomers, and η_0 the coefficient of the viscosity of the medium. Here, the term f , the fraction of uncondensed counterions, provides also a measure of polyion-counterion interaction in the absence of an electrolyte.

The interactions between the polyion and the counterions would, obviously, be modified 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

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

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

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

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 (κ) in presence of a salt to Eq. (14) provided κ_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.

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.^{93,102,104,131-134} In case of neutral polymer solutions, the reduced viscosity η_{sp}/c (defined as $\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$, where η is the viscosity of the solution, η_0 is the viscosity of the solvent alone and c is the (monomer) concentration of the polymer solution) is proportional to c . This well-known relation (known as the Huggins equation²) is used for determining the intrinsic viscosity $[\eta]$ simply by extrapolation of η_{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,^{135,136} 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 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,¹³⁷⁻¹⁴⁰ 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.¹⁴⁰ 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.¹⁴¹ Hodgson and Amis^{142,143} 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,^{144,145} poly (galacturonic acid) sodium salt,¹⁴⁶ sodium polystyrenesulfonate,^{138,147} sodium carboxymethylcellulose,¹⁴⁸ polysulfobetaines,¹⁴⁹⁻¹⁵² and polyelectrolytes with poly(*p*-phenylene) backbone¹⁵³ 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.¹⁵⁴ Later Cohen *et al.*^{138,139} derived a similar relation on the basis of the theory by Hess and Klein¹⁵⁵ 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.*¹⁵⁶ who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.¹⁵⁷ 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.*¹⁵⁶ 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.*¹⁵⁸ demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.¹⁵⁵ 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,

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

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

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

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

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

when ξ is >1 or ≤ 1 , respectively.

Antonietti *et al.*^{158,159} expressed the reduced viscosity for charged latex particles as:

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

in which $(\eta_{sp}/c)_{HK}$ 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.*¹⁵⁸ 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 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 η_{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^{2,160}

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

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 intrinsic viscosities can be determined in a more straightforward manner using the method of isoionic dilution.^{140,161} 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 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 method for the determination of intrinsic viscosity in a convenient manner, however, very little attention has been paid to this direction so far.^{102,104,131,140,145,161}

Interaction of Polyelectrolytes with Surfactants

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 in presence of simple electrolytes. 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.¹⁶²⁻¹⁶⁶ In particular, there have been significant research efforts focusing on the interactions between polyelectrolytes and oppositely charged surfactants in recent years.¹⁶⁶⁻¹⁸⁴ 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.^{185,186} While interactions between non-ionic polymers and ionic surfactants rely mainly on hydrophobicity,^{163,187} 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 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),¹⁸⁸ 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 in presence of an oppositely charged surfactant. With the increase in the surfactant concentration, a second transition known as the polymer-saturation point (*psc*) is obtained. Afterwords, 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**).

Experimental Efforts for Studying the Polyelectrolyte-Surfactant Interactions

The experimental efforts in this field were first devoted to the determination of binding isotherms,^{165,175,189-191} enthalpies of binding,^{172,192} and various thermodynamic and transport properties^{183,193} 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.^{194,195}

We will, however, give a brief account of the conductometry, tensiometry and viscometry to investigate the interactions between polyelectrolytes and surfactants since these techniques have been employed to study the behaviour of NaPSS-CTAB interactions in mixed solvent media in this dissertation.

Conductometry and Tensiometry

These are very powerful tools to study the polyelectrolyte-surfactant interactions. Conductometry provides the *cmc* of a pure surfactant solution as the intersection of two straight lines in the pre- and postmicellar regimes of the specific conductivity (κ) vs. surfactant concentration profile. In polyelectrolyte-surfactant systems, the conductometric patterns usually reveal three linear segments, 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*.^{174,196} 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 manifesting three breaks have also been reported.^{171,172} It should, however, be pointed out that Kogej and Skerjanc,¹⁸³ were able to identify two linear sections in the polyelectrolyte-surfactant specific conductivity (κ) 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 (Λ) 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 (γ) 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 γ - log[surfactant] curves for polyelectrolyte-surfactants, on the other hand, are not so simple. It was Jones¹⁹⁷ who studied the properties of mixed poly(ethylene oxide) (PEO)/sodium dodecylsulfate (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- $\log[\text{surfactant}]$ curve. This invariance of surface tension with $\log[\text{surfactant}]$ 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 $\log[\text{surfactant}]$ was reported by Prasad *et al.*¹⁷¹ 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 γ , 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 γ 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 γ 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.*¹⁹⁸ 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 VIII with reference to NaPSS-CTAB interaction in methanol-water mixed solvent media.

From a survey of the literature,¹⁶²⁻¹⁹⁸ 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 coililng/expansion of the polyion

chain in presence of surfactants in polymer-surfactant solutions were interpreted on the basis of these studies.

Viscometry

At low polyelectrolyte concentrations with no added salt, there is a semidilute unentangled solution regime that spans a wide concentration range. Addition of surfactant to such solutions lowers the viscosity dramatically.¹⁹⁹⁻²⁰⁶ Abuin and Scaiano¹⁹⁹ showed that this viscosity reduction is far stronger than the simple charge screening resulting from the addition of monovalent salt. Later, Plucktaveesak *et al.*²⁰⁷ introduced a simple viscosity model to predict the reduction of the viscosity of a polyelectrolyte solution upon addition of oppositely charged surfactant, based upon the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions.²⁰³ The model accounts for both changes in the effective chain length of the polyelectrolyte when it wraps around the exterior of the spherical micelles and changes in ionic strength resulting from surfactant and polyelectrolyte counterions. It is important to point out that Plucktaveesak *et al.*²⁰⁷ treat solutions with a stoichiometric excess of charged monomers relative to the oppositely charged added surfactant.

Plucktaveesak *et al.*²⁰⁷ introduced a simple model for the viscosity of polyelectrolyte solution in the presence of an added surfactant based on the scaling theory for the viscosity of unentangled semidilute polyelectrolyte solutions.³¹ A brief description of this approach is given below.

A Zimm model for the viscosity of dilute polyelectrolyte solutions has been proposed by Dobrynin *et al.*²⁰⁸ The specific viscosity (η_{sp}) is predicted to scale as the 4/5 power of the degree of polymerization (N) and to decrease as monovalent salt (with molar concentration c_s) is added:

$$\eta_{sp} \approx N^{4/5} \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/5} \quad c_p < c^* \quad (20)$$

where c_p is the molar concentration of monomers and other symbols have their usual significance. Hence, the term in the parentheses is the ratio of concentration of small ions from added salt ($2c_s$) to that of the free counterions from the polyelectrolyte ($f c_p$). The overlap concentration c^* is the crossover concentration between the dilute and semidilute regimes.²⁰⁸ A Rouse model for the viscosity of unentangled semidilute polyelectrolyte solutions has also been proposed by Dobrynin *et al.*²⁰⁸ This scaling theory predicts that the specific viscosity (η_{sp}) of the unentangled polyelectrolyte solutions is proportional to the

degree of polymerization N of the chains and decreases with addition of monovalent salt (with molar concentration c_s):

$$\eta_{sp} \approx N \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/4} \quad c^* < c_p < c_e \quad (21)$$

This equation holds for concentrations above the overlap concentration but below the entanglement concentration c_e .

As oppositely charged surfactant is added to a polyelectrolyte solution, the viscosity of the solution is lowered due to two effects. First, the polyelectrolyte loses some of its effective chain length in wrapping around the exterior of the surfactant micelles. It was assumed that one neutralized monomer is bound to each surfactant headgroup in the micelle. It was further assumed that neither the placement of charges along the polyion chain nor the fraction of neutralized monomers is altered by the interaction with the micelle. The polyion chain will wrap efficiently around the micelle, using a section of chain containing a number of neutralized monomers that is equal to the aggregation number of the micelle.

Now, if c is the concentration of the added surfactant, the fraction of polyelectrolyte monomers tied up with micelles is $c/(\alpha c_p)$, where α is the degree of neutralization, so the fraction of polyelectrolyte monomers that are free from micelles (proportional to the effective polyelectrolyte chain length) is $1 - c/(\alpha c_p)$. The second effect is that the ionic strength (the concentration of free ions) in solution increases as surfactant is added. These ions consist of polyelectrolyte counterions released upon interaction with the surfactant micelle, and counterions of surfactant molecules. It was assumed that, for each surfactant molecule bound to a polyelectrolyte monomer, there is effectively one salt molecule added to the solution, comprising the counterion of the polyelectrolyte monomer and the counterion of the surfactant. Since in most cases the critical aggregation concentration (cac) is very small, practically all added surfactant is bound to the polyelectrolyte, making the effective salt concentration c , the concentration of added surfactant. The number density of free polyelectrolyte counterions also diminishes as surfactant is added because the fraction of the chain bound to micelles no longer has free counterions. It was assumed that the fraction of free counterions on the remaining sections of chain is the same as without added surfactant, making the number density of free counterions $fc_p[1 - c/(\alpha c_p)]$. The ratio of salt ions to free polyelectrolyte counterions ($2c_s/fc_p$) in Eqs. (20) and (21) becomes $2c/(fc_p[1 - c/(\alpha c_p)])$.

Eqs. (20) and (21) are, therefore, modified to describe the viscosity of polyelectrolyte solutions as oppositely charged surfactant is added:

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]^{4/5} \left[1 + \frac{2c}{fc_p \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]} \right]^{-3/5}$$

$c_p < c^*$ (22)

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p} \right) \right] \left[1 + \frac{2c}{fc_p \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]} \right]^{-3/4}$$

$c^* < c_p < c_e$ (23)

$\eta_{sp}(c)$ and $\eta_{sp}(0)$ are the specific viscosities of polymer with and without added surfactant, respectively.

Eq. (23), however, needs modification for surfactant concentration above the critical aggregation concentration and the relevant equation is

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \delta \left(\frac{c - cac}{\alpha c_p} \right) \right] \left[1 + \frac{2c}{fc_p \left[1 - \delta \left(\frac{c - cac}{\alpha c_p} \right) \right]} \right]^{-3/4}$$

$c^* < c_p < c_e$ and $c > cac$ (24)

The critical aggregation concentration is cac and the fraction of micelle headgroups associated with polyelectrolyte is δ .

This model has been successfully employed²⁰⁷ to describe quantitatively the viscosity behaviour of a number of polyelectrolyte-oppositely charged surfactant systems. e.g.,

- i) dodecyltrimethylammonium bromide (C₁₂TAB) - polyacrylic acid systems with various neutralization extents (α) and chain lengths of the polyelectrolyte,

- ii) cetylpyridinium chloride ($C_{16}PC$) - sodium polyacrylate (NaPAA),
- iii) $C_{16}PC$ - sodium polystyrenesulfonate (NaPSS),
- iv) $C_{12}TAB$ - a random copolymer of 75% acrylamide and 25% sodium 2-acrylamido-2-methylpropanesulfonate, and
- v) $C_{12}TAB$ - a random copolymer of 90% acrylamide and 10% sodium 2-acrylamido-2-methylpropanesulfonate.

This model thus provides a universal description of viscosity for any oppositely charged polyelectrolyte/surfactant systems having spherical micelles. Breakdown of this model, therefore, gives a clue about the formation of other phases e.g., lamellar phases, cubic phases of spherical micelles etc.²⁰⁹⁻²¹¹

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 explore this issue 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. In the present investigation, we have, therefore, utilized conductometry and viscosimetry to study the solution behaviour of NaPSS and conductometry, viscosimetry, and tensiometry to study the interaction between NaPSS and a cationic surfactant CTAB in methanol-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.²¹² 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 operative in the case of oppositely charged polyelectrolyte and surfactants in solutions are strong interactions due to the contributions 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 micelle 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. Thus electrostatic interactions play an important role in controlling the solution behaviour of polyelectrolytes in absence as well as in presence of an oppositely charged surfactant, which, in turn, is intimately related to the relative permittivity of the solvent media. Now, use of a series of mixed solvents corresponds to the systematic change in the relative permittivity of the media and thus provides an opportunity to study these interactions from a more general point of view. In this study, the mixed solvent methanol-water has been used. Methanol-water is a popular mixed solvent and has been extensively studied.^{100,213-224} These mixed solvents are of interest because although the two solvents are fully miscible at room temperature, the components have very different chemical natures. Hydrogen bonding liquid methanol is the simplest amphiphile functionalized with hydrophobic (-CH₃) and hydrophilic (-OH) groups. Understanding of the solvation properties of methanol as it relates to the disposition of hydrophobic/hydrophilic groups in polar or nonpolar solvents is of fundamental importance in biological and chemical sciences because amphiphiles are essential constituents making up cell membranes and are also extensively used in chemical industries as micelles (e.g., detergent action). In fact, the eccentric properties associated with water-alcohol mixtures have been the focus of numerous scientific investigations and significant technological applications.²¹³⁻²²⁴ It would, therefore, be interesting to investigate the behaviour of a polyelectrolyte both in absence and in presence of an oppositely charged surfactant in these mixed solvents.

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