

Studies on the Behaviour of Polyelectrolytes &  
their Interaction with Small Ion & Surfactant  
in Mixed Solvent

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*By  
Debapratim Ghosh, M.Sc.*

*DEPARTMENT OF CHEMISTRY*  
**UNIVERSITY OF NORTH BENGAL**  
DARJEELING 734 013, INDIA

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Dated: 29/12/09  
Department of Chemistry  
University of North Bengal  
Darjeeling, 734 013

*Debapratim Ghosh*  
(DEBAPRATIM GHOSH)

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## Preface

### Scope and Object of the Work

Since the birth of polymer science, polyelectrolytes have been the subject of extensive investigation. They still continue to be a very active area of research in a variety of fields *e.g.*, chemistry, physics, biology, medicine, materials science and nanotechnology. The widespread interest in the area of polyelectrolytes stems from the scientific curiosity in understanding their behaviour and also from their enormous potential in commercial applications. Polyelectrolytes have been utilised to assemble nanostructured materials with desired properties. Potential applications in medicine and biomedical engineering are also being vigorously pursued. Complexes of polyelectrolytes with conjugated polymers such as polythiophenes and polyanilines are being used commercially as conducting coatings. These are widely used in industry as surface-active agents for water treatment and oil-spill treatment. These also find applications in the industrial production of personal care products, cosmetics, pharmaceuticals, biosensors, surfactants, absorbents, ion exchange resins, stabilizers, adhesives, paints, papers etc. A very promising and emerging area of application of polyelectrolytes is the assembly of thin films of novel materials. When polyelectrolytes and surfactants are present together in solution either inherently or by design, there can be significant interaction between them that can be important in such long-established areas as mineral and material processing, enhanced oil recovery, detergency and paint and cosmetic formulation. More interest also stems from the potential for utilising the microstructural environment of polyelectrolyte-surfactant complexes in applications such as control of chemical reactivity, drug delivery, solar energy conversion and isotope separation. Accounts of some of the important applications of polyelectrolytes are available in various books and reviews.<sup>1-17</sup>

Physicochemical properties of polyelectrolyte solutions have been studied for several decades, but several of them have not yet found a satisfactory theoretical explanation. In many cases a qualitative understanding is available, but a quantitative understanding is still awaited. For others, the origin of the phenomena observed remains partly obscure, indicating that the present treatment of the polyelectrolyte behaviour is incomplete and that some fundamental new views are required to gain a full understanding. Keeping in view of widening fields of applications based on the specific properties of the polyelectrolytes, it, thus, appears that the situation is far from satisfactory.

In recent years, the study of polyelectrolytes has seen a revival stimulated by the use of newly available experimental techniques and the introduction of new theoretical approaches. Although new insight has been gained, no real breakthrough has been realized so far and much remains to be done.

The study of polyelectrolyte solutions has been conducted very extensively in aqueous solutions.<sup>13-22</sup> This is partly because many polyelectrolytes, usually with high charge densities, are difficult to dissolve in solvents besides water. Moreover, because of the great interest in the naturally occurring polyelectrolytes such as proteins, nucleic acids, and polysaccharides in aqueous medium, the behaviour of these species in aqueous solutions has become a main subject of study.<sup>13-26</sup>

The main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between the 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 the expansibility of the polymer chains, whereas the second is not only reflected in counterion binding but also in the amount of solvation and the solvent structure in the vicinity of polyelectrolytes. Both of these factors are related to the relative permittivity of the solvent media. Use of a series of mixed solvents corresponds to a systematic change in the relative permittivity of the media and hence allows us to study the behaviour of polyelectrolyte solutions from a more general point of view.

The present dissertation, therefore, aims at elucidating the behaviour of a selected polyelectrolyte (sodium polstyrenesulfonate, NaPSS) in acetonitrile-water mixed solvent media using different experimental techniques with special reference to its interaction with small ions and surfactant ions furnished by the surfactant cetyltrimethylammonium bromide (CTAB).

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## Chapter I

### Summary of the Works Done

In this dissertation, a systematic and comprehensive study of the solution behavior of a polyelectrolyte in mixed solvent media has been carried out from electrical conductivity, viscosity, and density measurements in order to elucidate the behaviour of various types of interactions prevailing in solution. Influence of this polyelectrolyte on the aggregation behavior of a surfactant in mixed solvents have also been investigated using conductometry and tensiometry.

Binary mixtures of acetonitrile and water have been chosen as the solvent system in the present study.

NaPSS is used as the polyelectrolyte species and CTAB as the surfactant molecule in this investigation. NaPSS is an important industrial polymer with a wide range of applications, for example as a superplasticizer in cement, as a dye improving agent for cotton, as proton exchange membranes in fuel cells, as a medication for treating abnormally high potassium levels.<sup>1-4</sup> So the present study is expected to help extend the fruitful use of this class of polymers.

The present dissertation has been divided into nine chapters.

Chapter I (the present chapter) gives a brief account of the works done in this dissertation.

Chapter II forms the background of the present work. After presenting a brief review of the notable works in the field of polyelectrolyte solution chemistry and polyelectrolyte-surfactant interactions, properties like conductance, viscosity, apparent and partial molar volumes of polyelectrolytes solutions, and conductance and surface tension in connection with polyelectrolyte-surfactant interactions have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion interactions and polyion-surfactant interactions were discussed with special reference to the influence of these interactions on the macroion conformations and the extent of counterion dissociation in polyelectrolyte solutions.

Chapter III describes the experimental techniques used to obtain the results presented in the dissertation. Purifications of the chemicals used have also been discussed. (Appendix provides an account of the determination of the limiting equivalent conductivity of sodium ion in acetonitrile-water mixed solvent media.)

Chapter IV reports the electrical conductivities of solutions of NaPSS in acetonitrile-water mixed solvent media containing 20 and 40 volume percent of acetonitrile at 308.15, 313.15, and 318.15 K in absence of an added salt. The applicability of the Manning theory<sup>5</sup> for conductivity of salt-free polyelectrolyte solutions is examined and a major deviation from the theory was observed. Possible reasons for this deviation have been discussed. The effects of temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fractions of uncondensed counterions were also investigated. The applicability of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et. al.*<sup>6</sup> using the scaling theory approach to the experimental results of electrical conductivity of NaPSS in acetonitrile-water mixtures was also tested. We have been able to quantitatively describe the electrical conductivity behaviour of NaPSS in acetonitrile-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

In Chapter V, the electrical conductivities of NaPSS in acetonitrile-water mixed solvent media containing 10, 20, and 40 volume percent of acetonitrile at 308.15, 313.15, and 318.15 K in presence of sodium chloride (NaCl) have been reported. Influence of this salt on the electrical conductivity behaviour of NaPSS is discussed. The results obtained highlighted the importance of several factors *e.g.*, the electrophoretic countercurrent, solvodynamic interactions, changing polyion conformation and the apparent charge upon the polyion etc. in these solutions.

In Chapter VI, the intrinsic viscosities of NaPSS in water and in three acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15, and 318.15 K using the isoionic dilution technique have been obtained. The influences of the medium, the temperature, and the total ionic strength on the intrinsic viscosities as well as on the Huggins constants have been interpreted from the points of view of the solvodynamic and thermodynamic interactions prevailing in the polyelectrolyte solution under investigation.

Chapter VII reports the viscosities of NaPSS in acetonitrile-water mixed solvent media both in absence and in presence of NaCl with varying concentrations. Effects of solvent composition have also been examined. The variations of the intrinsic viscosity and

the Huggins constant with the solvent medium have been used to interpret the variation in the coiling of the polyion chain and counterion condensation.

Chapter VIII describes the partial molar volumes of NaPSS in acetonitrile-water media containing 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15, and 318.15 K. This study indicates that in acetonitrile-water mixed solvent media, the counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Moreover, the polyion is found to govern the volumetric behaviour of the polyelectrolyte as a whole in these solutions. The predominance of the combined influence of the polyion-solvent electrostrictive interactions and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium was observed. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

Chapter IX reports the aggregation behaviour of CTAB both in absence and in presence varying concentration of NaPSS in acetonitrile-water mixed solvent media at 308.15, 313.15, and 318.15 K. NaPSS induced self-aggregation of CTAB at a concentration much lower than its *cmc* values in the mixed solvent media. The system has evidenced different kinds of interacting features corresponding to polyelectrolyte-induced aggregate formation, CTAB aggregate-NaPSS binding in bulk, CTAB-NaPSS binding at the interface, and free micelle formation in solution. The critical aggregation concentrations (*cac*), polymer saturation concentrations (*psc*), and apparent critical micellar concentrations (*cmc*\*) for NaPSS-CTAB interactions have been determined from tensiometry and conductometry. Good agreement between the values obtained from these two techniques was found. The results have been discussed in terms of various interactions prevailing in the present system.

The dissertation ends with some concluding remarks in Chapter X.

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## 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

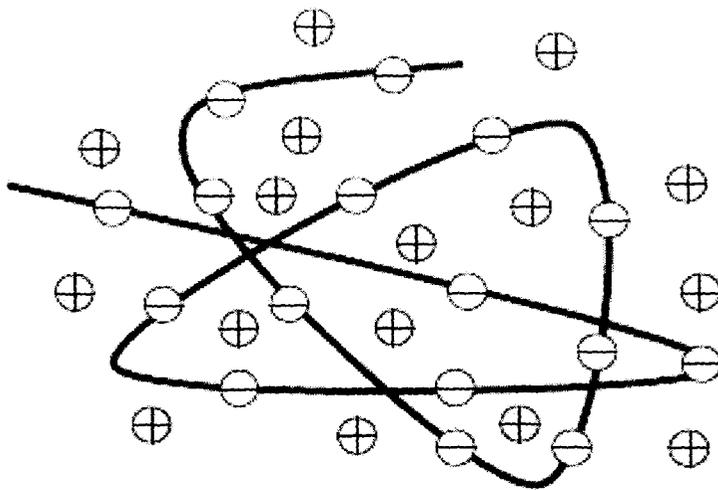
macromolecules. The behaviour of polyelectrolytes is also governed by such factors as the solution pH, nature of the ions, molecular weight, solvent polarity, temperature etc. Moreover the presence of the multivalent counterions significantly influences the structure and dynamics of the polyelectrolyte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

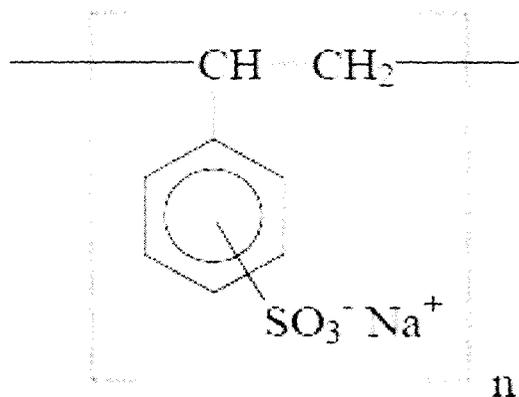
Based upon the molecular architecture, polyelectrolytes have been divided into two important categories, namely linear and branched polyelectrolytes. In linear polyelectrolytes, a large number of atoms are connected together to form the backbone chain. Although in a topological sense the backbone is 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

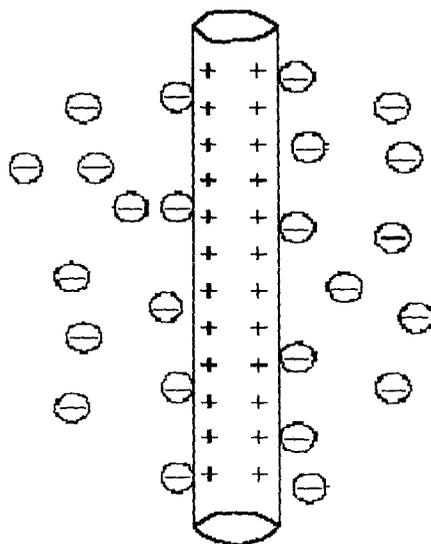


**Figure 1b.** An example of a flexible polyelectrolyte: sulphonated polystyrene with sodium counterions.

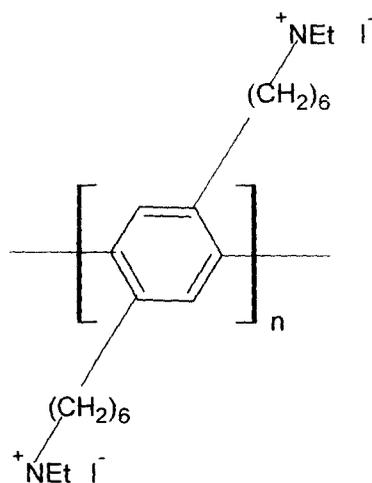
intermolecular Coulombic interactions determine the solution properties of these polyelectrolytes. An example of this type of polyelectrolyte is poly (*p*-phenylene) with iodine counterions (Figure 2b). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as, DNA, RNA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



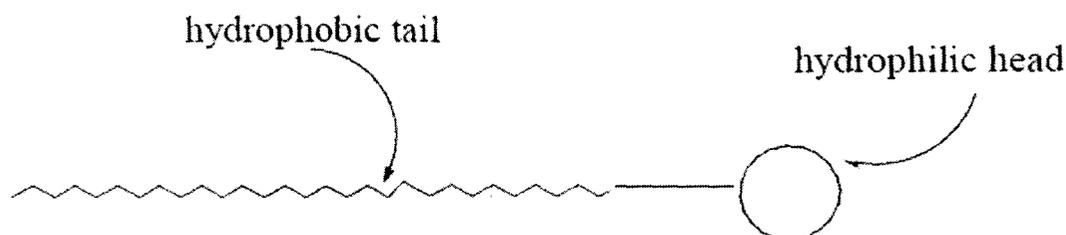
**Figure 2b.** An example of a rigid rod-like polyelectrolyte: poly (*p*-phenylene) with iodine counterions.

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.

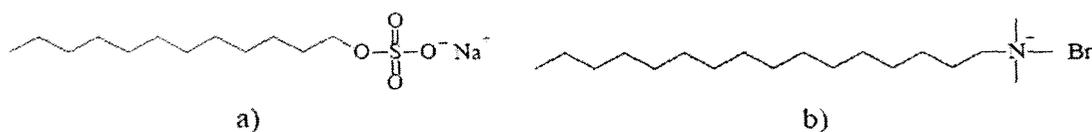
The behaviour of surfactants in aqueous solutions is determined by their tendency to move their hydrophobic part away from the solution and their hydrophilic part towards the solution. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates 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***

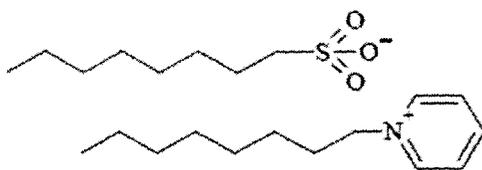
Surfactants can be classified according to their physical properties or functionalities. The following is the most common classification based on the nature of the head group.

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).

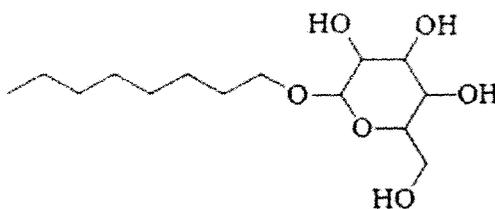


**Figure 5.** A symmetric catanionic surfactant, octylpyridinium octanesulphonate (OPOS).

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



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>

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

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

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

Here  $X$  is the ratio of the equivalent polyelectrolyte concentration ( $c_p$ ) to the equivalent salt concentration ( $c_s$ ), and  $\xi$  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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## Chapter III

### Experimental

#### Chemicals

##### *Sodium Polystyrenesulfonate (NaPSS)*

The sodium salt of polystyrenesulfonic acid (NaPSS) with a molecular weight of 70,000 and a degree of sulfonation of 1.0 (Aldrich Chemical Company) was purified by dialysis.<sup>1,2</sup> The molecular weight reported by the manufacturer agreed well with that determined in the present study obtained in presence of 0.05 M sodium chloride (NaCl) at 298.15 K using the Mark-Houwink relationship,<sup>3</sup>  $[\eta] = 1.39 \times 10^{-4} M^{0.72}$ , where  $[\eta]$  is the intrinsic viscosity, and  $M$  is the average molecular weight. The absorption coefficient of the NaPSS solutions used at 261 nm, which is considered to be a characteristic indicator of the sample purity,<sup>2</sup> is found to be  $400 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ . Spectroscopic examination of the polyelectrolyte sample using this criterion was employed periodically to substantiate the sample purity.

##### *Cetyltrimethylammonium Bromide (CTAB)*

Cetyltrimethylammonium bromide was purchased from Aldrich Chemical Company. The surfactant was recrystallised several times until no minimum in the surface tension-concentration plot was observed and its critical micellar concentration (cmc) agreed with the literature value.<sup>4</sup>

##### *Sodium Chloride (NaCl)*

Sodium chloride (Fluka) was of purum grade; this was dried *in vacuo* for a prolonged period immediately before use and was used without further purification.

## **Solvents**

### ***Acetonitrile***

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentaoxide and redistilled over calcium hydride. The purified solvent had a density of  $0.76570 \text{ g cm}^{-3}$  and a coefficient of viscosity of  $0.3126 \text{ mPa}\cdot\text{s}$  at  $308.15 \text{ K}$ ; these values are in good agreement with the literature values.<sup>5</sup>

### ***Water***

Triply distilled water was used for the preparation of the experimental solutions. Water was first deionized and then distilled from an all glass distilling set using alkaline  $\text{KMnO}_4$  solution. The distilled water was then distilled twice. Precautions were taken to prevent contaminations from  $\text{CO}_2$  and other impurities. The triply distilled water which had a specific conductance of less than  $10^{-6} \text{ S}\cdot\text{cm}^{-1}$  at  $308.15 \text{ K}$  was used for the preparation of the solutions.

## **Preparation of the Mixed Solvents**

The acetonitrile-water mixed solvents were prepared accurately by mixing requisite amounts of acetonitrile and water by mass. The physical properties namely the densities ( $\rho_0$ ), the coefficients of viscosities ( $\eta_0$ ) and the relative permittivities ( $D$ ) of these mixed solvents used at  $308.15$ ,  $313.15$ , and  $318.15 \text{ K}$  are reported in Table 1. The relative permittivities of acetonitrile-water mixtures at the experimental temperatures were obtained with the equations as described in the literature<sup>6</sup> using the literature density and relative permittivity data of the pure solvents<sup>5,7</sup> and the densities of the mixed solvents given in Table 1. Also included in this table are the limiting equivalent conductivities of sodium ion ( $\text{Na}^+$ ) in acetonitrile-water mixtures (*cf.* Appendix).

## **Methods**

### ***Conductance Measurements***

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of  $2000 \text{ Hz}$  using a dip-type cell with a cell constant of  $1.15 \text{ cm}^{-1}$  and having an uncertainty of  $0.01$  percent. The cell was calibrated by the method of Lind and co-

workers<sup>8</sup> using aqueous potassium chloride solution. The measurements were made in a water bath maintained within  $\pm 0.005$  K of the desired temperature. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

### ***Density Measurements***

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at the experimental temperatures with deionized distilled water, methanol and acetonitrile. The precisions of the density measurements were always within  $3 \times 10^{-5} \text{ g.cm}^{-3}$ . The measurements were performed in a water bath which was maintained within an accuracy of 0.005 K of the desired temperature by means of an electronic relay and a contact thermometer.

### ***Viscosity Measurements***

The viscometric measurements were performed at 308.15, 313.15, and 323.15 K using a Schultz-Immergut-type viscometer<sup>9</sup> with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within  $\pm 0.005$  K of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.<sup>10,11</sup> Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

### ***Surface Tension Measurements***

The surface tensions of the surfactant solutions were measured at 308.15, 313.15, and 318.15 K using a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was briefly heated by holding it above a

Bunsen burner until glowing. The measurements were made in a thermostat maintained within  $\pm 0.005$  K of the desired temperature.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

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**Table 1.** Properties of Acetonitrile-Water Mixtures Containing 10, 20, and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K and the Limiting Conductivity Values of Sodium Ion in the Mixed Solvent Media

$T$ (K)	$\eta_0$ (mPa s)	$\rho$ (g cm <sup>-3</sup> )	$D$	$\lambda_{\text{Na}}^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )
<b>10 percent acetonitrile</b>				
308.15	0.8766	0.98096	72.15	58.81
313.15	0.7622	0.97893	69.89	65.15
318.15	0.6773	0.97625	68.27	70.50
<b>20 percent acetonitrile</b>				
308.15	0.9067	0.96485	67.94	56.21
313.15	0.7833	0.96200	66.38	62.77
318.15	0.6984	0.95912	64.84	68.03
<b>40 percent acetonitrile</b>				
308.15	0.8200	0.92362	60.07	51.50
313.15	0.6803	0.91730	58.87	57.84
318.15	0.5611	0.91542	57.32	65.34

## Electrical Conductivity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media: Experiment and Data Analysis Using the Manning Counterion Condensation Model and the Scaling Theory Approach

### Introduction

Polyelectrolytes are polymers with ionizable groups which in polar solvent media dissociate into a polyion and counterions of opposite charge.<sup>1-3</sup>

The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory.<sup>4-9</sup> Within this model, the polyion is represented as an infinitely long charged line, small ions (counterions) are assumed to form an ionic atmosphere whose density depends on the frame of the polyion and their interactions with the charged polyions are purely coulombic, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye-Hückel approximation. The solvent is assumed to be a dielectric continuum characterized by a spatially uniform relative permittivity  $\epsilon$ . Interactions among polyions are neglected, the theory being addressed to highly diluted solutions.

Generally, the equivalent conductivity of polyelectrolyte solutions is given by<sup>4</sup>

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (1)$$

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 fraction of uncondensed counterions.

According to the Manning counterion condensation theory, polyelectrolytes have been characterized by a linear charge density parameter defined by<sup>4,7,9</sup>

$$\xi = e^2 / \epsilon k_B T b \quad (2)$$

where  $e$  is the protonic charge,  $\epsilon$  the relative permittivity of the medium,  $k_B$  the Boltzmann constant and  $T$  the absolute temperature and  $b$  is the contour distance per unit charge. This theory states that if  $\xi > 1$ , enough counterions condense on to the polyion chain to yield the

critical value  $\xi = 1$ . If, on the other hand,  $\xi < 1$ , ionization takes place to reach this critical value.

Considering the electrophoretic and relaxation contributions to the equivalent conductivity,  $\lambda_p$ , Manning<sup>4</sup> theoretically derived the equivalent conductivity of a polyion with counterions each bearing a charge of  $z_c$

$$\lambda_p = 279A|z_c|^{-1}|\ln \kappa a|/[1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|] \quad (3)$$

where  $a$  is the radius of the cylindrical polymer backbone, while

$$A = \varepsilon k_B T / 3\pi\eta_0 e \quad (4)$$

with  $\eta_0$  being the coefficient of viscosity of the solvent. In Eq. (3),  $\kappa$  is the Debye screening constant, which is defined by

$$\kappa^2 = (4\pi e^2 \xi^{-1} c |z_c|) / (\varepsilon k_B T) \quad (5)$$

where  $c$  is the stoichiometric equivalent polyion concentration.

Within this model, the equivalent conductivity ( $\Lambda$ ) is given by Eq. (1) in conjunction with Eq. (3) with  $f$  being defined as

$$f = 0.866 / \xi \quad (6)$$

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 Wandrey and Hunkeler<sup>10</sup> and Bordi *et. al.*<sup>11</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>4</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>12</sup> and Szymczak *et. al.*<sup>13</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>12</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 70000 and 500000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the increase after the minimum was passed could not be explained. It was concluded that the applicability of the Manning theory is questionable for a concentration range where chain coiling is probable. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonate in semidilute solutions were carried out by Szymczak *et. al.* at 298.15 K.<sup>13</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>14, 15</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>16</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>17</sup>

Wandrey *et al.*<sup>18</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>19</sup> compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4000, 167000 for both the dilute and semidilute regimes. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polymer molecular weight. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molecular weight sample is hardly surprising, since these data are all above  $c^*$ , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molecular weight sample is noteworthy since these data are all below  $c^*$ .

In a study on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-co-(vinyl pyrrolidone)], Rios<sup>20</sup> confined the attention below the overlap concentration. Whereas the Manning model predicts a slow but monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration, a maximum was observed experimentally in each of these three cases. Although, the agreement between the experiment and theory is generally poor, theoretical curves approach the experimental ones for the lithium and sodium salts over a very narrow concentration range for very dilute solutions.

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

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*<sup>21</sup> using the scaling description proposed by Dobrynin *et al.*<sup>22</sup> for the configuration of a polyelectrolyte chain.

In 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  $q_\xi = zefg$  ( $z$  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  $Q_p = N_\xi q_\xi = zefg N_\xi$ . 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  $\xi_0$ .

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

$$\lambda_p = (Fzefc\xi_0^2 / 3\pi\eta_0) \ln(\xi_0 / \xi_e) \quad (7)$$

where  $F$  is the Faraday number and the other symbols have their usual significance.

Thus according to this model the equivalent conductivity of a polyelectrolyte solution is given by Eq. (1) with the  $\lambda_p$  value obtained from Eq. (7).

Within this model, the parameter  $f$  - that defines the fraction of uncondensed counterions in the Manning sense - has been treated as an adjustable one. 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, the Colby model 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>11, 19, 21</sup> and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify concentration regimes differing in the fractions of uncondensed counterions.<sup>23</sup> This model, however, has not been applied to polyelectrolyte solutions in solvents besides water.

Although studies on the polyelectrolyte conductivity in salt-free aqueous solutions are now plentiful at 298.15 K,<sup>10, 11</sup> not much attention was paid to such studies dealing with temperature dependence.<sup>16, 17, 19, 24, 25</sup> The situation worsens in mixed solvent media. Only a few investigations has so far been made<sup>26-28</sup> at a given temperature. To our knowledge, there has been no attempt to study the conductivity behaviour of salt-free polyelectrolyte solutions in mixed solvent as a function of temperature except those reported from our laboratory.<sup>29-31</sup> In our earlier investigations on polyelectrolyte conductivity in mixed solvent media, we have demonstrated the failure of the Manning model for these systems. Here we present a study on the electrical conductivity of the semidilute solutions of sodium polystyrenesulfonate in

acetonitrile-water mixed solvent media at different temperatures. We have also observed inapplicability of the Manning model here and have therefore analysed the data on the basis of the scaling theory. This is, in fact, the first report on the application of the scaling theory approach to semidilute polyelectrolyte conductivity in mixed solvent media. The influences of concentration, medium, and temperature on the extent of uncondensed counterions as well as on the mobility of the polyelectrolyte species have also been investigated.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. Triply distilled water with a specific conductance of less than  $10^{-6}$  S cm<sup>-1</sup> at 308.15 K was used for the preparation of the solvent mixtures. The physical properties of acetonitrile-water mixtures used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1 of Chapter III.

Also included in this table are the limiting equivalent conductivity of the counterion (Na<sup>+</sup>),  $\lambda_c^0$ , in 20 and 40 volume percent of acetonitrile-water mixtures which were reported earlier<sup>32</sup> (*cf.* Appendix).

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was 70 kDa.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz with negligible polarization effects using a dip-type cell with a cell constant of 1.15 cm<sup>-1</sup> and having an uncertainty of 0.01%. The measurements were made in a water bath maintained within  $\pm 0.005$  K of the desired temperature. The details of the experimental procedure have been described earlier.<sup>33</sup> Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium ( $\kappa_0$ ) from those of the polyelectrolyte solutions ( $\kappa$ ).

In order to avoid moisture pickup, the experimental solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates and the results were averaged.

## Results and Discussion

### *Experimental Equivalent Conductivity*

The experimental equivalent conductivities ( $\Lambda$ ) for sodium polystyrenesulfonate as a function of the square root of the polyelectrolyte concentration ( $\sqrt{c}$ ) in two acetonitrile-water mixed solvent media (containing 20 and 40 vol% of acetonitrile) at 308.15, 313.15, and 318.15 K over the entire concentration range investigated are shown in Figures 1 and 2. From these figures, it is evident that the present species demonstrates typical polyelectrolyte behavior in which the equivalent conductivities exhibit a slight increase with decreasing concentration. Equivalent conductivities of sodium polystyrenesulfonate have been reported earlier in pure water as a function of polyelectrolyte concentration and temperature.<sup>24</sup> Davydova *et. al.*<sup>25</sup> reported the temperature dependence of the mean charge spacing ( $b$ ) for of aqueous sodium polystyrenesulfonate solutions; but the experimental equivalent conductivity values were not available and hence a comparison with our results is not possible. A comparison of our results with those reported in reference<sup>24</sup> indicates that the  $\Lambda$  values in acetonitrile-water mixtures are always higher than the corresponding values in water. This may be ascribed to greater solvation of the sodium counterions in aqueous solution.

The effects of temperature on the equivalent conductivity values are directly evident from the Figures 1 and 2, where in a given solvent medium  $\Lambda$  values are found to increase with temperature over the entire concentration range. At each temperature, however, the  $\Lambda$  values are found to decrease with decreasing relative permittivity in going from 20 percent to 40 percent acetonitrile-water mixtures over the entire concentration range investigated as illustrated in Figures 1 and 2. This is quite expected because as the relative permittivity of the medium decreases, interaction between polyion and counterions is expected to increase with concomitant lowering in the mobilities of the conducting species and hence in that of the polyelectrolyte as a whole. Increasing temperature, on the other hand, is expected to increase the mobility as manifested in these figures.

### *Comparison with Manning Counterion Condensation Theory*

Now we will compare the experimental  $\Lambda$  values with those calculated using the Manning theory. It may be mentioned that no attempt was made earlier to correlate the experimental equivalent conductivities of sodium polystyrenesulfonate obtained at different temperatures in aqueous solutions with the Manning predictions.<sup>24,25</sup> The charge density

parameters ( $\xi$ ) were calculated from Eq. (2) using the literature value for the length of the monomer unit having one charged group ( $b$ )<sup>34</sup> and are reported in Table 1. The theoretical values of  $\lambda_p$  and hence of  $\Lambda$ , are dependent on  $a$ , the radius of the polyion cylinder. For the radius of the assumedly rod-like polymer cylinder, we used a value of  $8 \text{ \AA}$  for the present analysis.<sup>34</sup>

Graphical representation of the theoretical predictions (solid lines) based on this model along with the experimental  $\Lambda$  values (points) are included in Figures 1 and 2 at 308.15, 313.15, and 318.15 K in acetonitrile-water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. The same situation of negative deviation<sup>13, 17</sup> as well as positive deviation<sup>20, 35</sup> from the experimental values was also noticed for other polyelectrolyte solutions. The discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies Eq. (5).

### ***Comparison with the Scaling Theory Approach***

The reason for the failure of the Manning model in the present investigation can be understood if one estimates the overlap concentration ( $c^*$ ) for the polymer chain investigated using the following equation

$$c^* = 1/N_{\Lambda}L^2a \quad (8)$$

where the symbols have their usual significance. It is observed that the polymer solutions used in the present study are essentially in the semidilute regime ( $c > c^* \approx 0.001 \text{ eqiv L}^{-1}$ ) where the Manning limiting law does not apply.

We, therefore, have taken the recourse of the approach proposed by Colby *et. al.*<sup>21</sup> for semidilute polyelectrolyte solutions, for the analysis of our conductivity data.

Since the present acetonitrile-water mixtures are poor solvent for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule, we use a value of  $5 \text{ \AA}$  as the effective monomer size ( $b$ ) as suggested by Colby *et. al.*<sup>21</sup>

Under poor solvent condition, the electrostatic blob size ( $\xi_c$ ) and the correlation blob size ( $\xi_0$ ) are given by<sup>21</sup>

$$\xi_e = b(A^2 / \xi)^{1/3} \quad (9)$$

$$\xi_0 = (cb)^{-1/2} (A^2 / \xi)^{1/3} \quad (10)$$

In Figures 1 and 2, the predictions of the Colby model (dashed lines) for the semidilute regime have been compared with the experimental data. The Colby model is found to reproduce the experimental results here quite satisfactorily.

The agreement of the theory with the experimental data is particularly significant considering that the theory requires only one adjustable parameter, namely the fraction of uncondensed counterions ( $f$ ), to describe the experimental results. A closer look at the Figures 1 and 2 as well as the standard deviations of the fits recorded in Table 2, however, reveal that although the scaling theory approach provides a dramatic improvement over the Manning model with a constant level of counterion condensation with polyelectrolyte concentration, the usual assumption that the effective charge on a polyion chain is independent of the polymer concentration is no longer valid for the system under investigation.

The measured fraction of uncondensed counterions and its dependence on temperature and relative permittivity

Since the fractions of uncondensed counterions ( $f$ ) were found to vary with the polymer concentrations, we have calculated the fractions from our conductivity data using Eq. (1) in conjunction with Eq. (7). The concentration dependence of  $f$  thus obtained is shown in Figures 3 and 4. These figures demonstrate that the fraction of the uncondensed counterions does not remain fixed over the concentration range investigated in the present study (3-5% increase in the fraction of uncondensed counterions was observed).

The measured fraction of uncondensed counterions is found to decrease with decreasing relative permittivity (*i.e.*, with increasing acetonitrile content of the mixed solvent media) at each temperature (Figures 3 and 4). Since decreasing relative permittivity should result in a greater interaction between the polyion and counterions, the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower - as has been observed in the present study.

The influence of temperature on the  $f$  value in the present mixed solvent media is, at first sight, rather perplexing. For any given mixed solvent system, the fraction of

uncondensed counterions is found to decrease with increasing temperature (Figures 3 and 4) which apparently contradicts the experimental observation in Figures 1 and 2 where the equivalent conductivity increases with temperature in each of the mixed solvent medium investigated. This can be ascribed to a change in solvation and condensation behavior of counterions upon changing the temperature. Raising the temperature has the effect of decreasing ionic solvation for the counterions which results in an increase of counterion condensation on the polyion chain. This is reflected in the decreasing fraction of uncondensed counterions at higher temperatures. Still, the equivalent conductivities increase with increasing temperature due to a temperature-induced increase in the speed of the ions in a lower viscous medium at higher temperatures.

## Conclusions

An investigation on electrical conductivity of salt-free solution of an anionic polyelectrolyte - sodium polystyrenesulfonate - in acetonitrile-water mixed solvent media has been presented as a function of polymer concentration and temperature. The equivalent conductivities are found to increase with increasing temperature over the entire concentration range in a given mixed solvent medium whereas these are found to decrease as the relative permittivity of the medium decreases. The conductivity theory, proposed by Manning, for salt-free polyelectrolyte solutions, was applied to analyze the experimental data. The measured values of equivalent conductivity could not be quantitatively described by the Manning counterion condensation theory. This discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model valid only at infinite dilution that underlies this theory. A recent model proposed by Colby *et. al.*<sup>21</sup> based on scaling considerations for the configuration of a polyelectrolyte chain in semidilute solution has also been tested and the results derived from this model are found to be quantitatively consistent with the experimental observations. A closer look, however, reveals that although the scaling theory approach on the basis of a constant level of counterion condensation provides a dramatic improvement over the Manning model, the fraction of the uncondensed counterions does not remain fixed over the concentration range investigated in the present study. The influences of temperature and the relative permittivity of the medium on the equivalent conductivity as well as the fractions of uncondensed counterions were also investigated.

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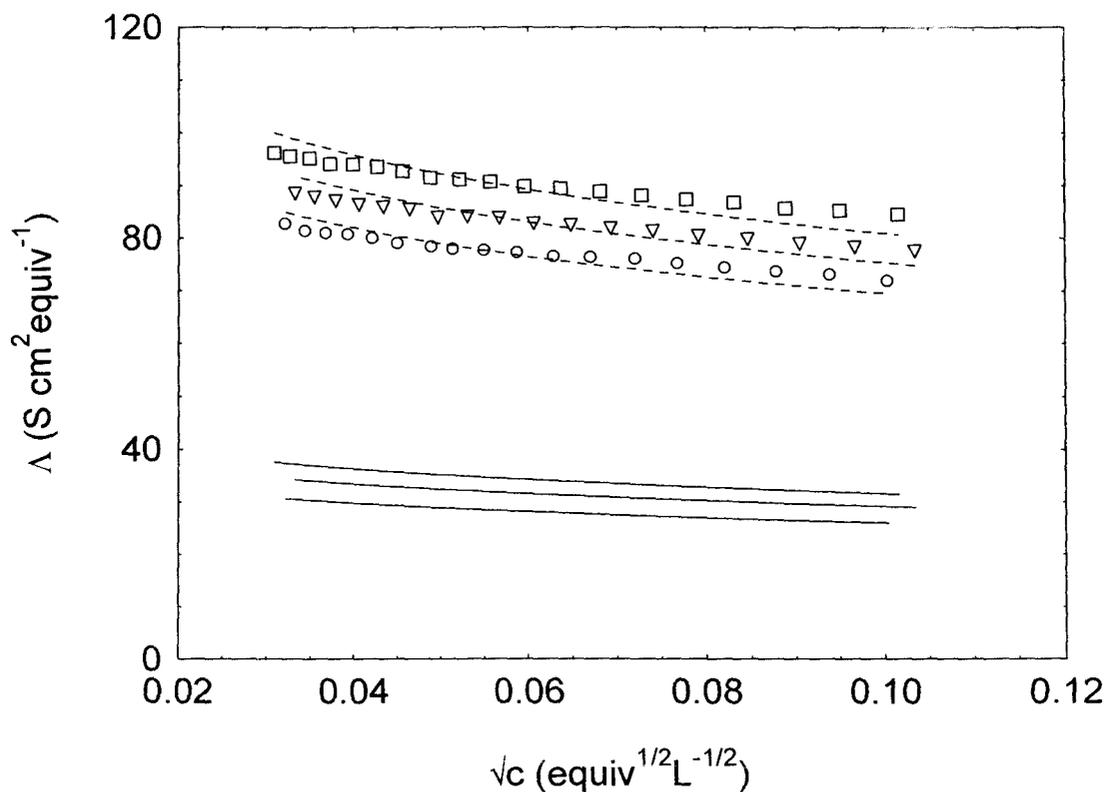
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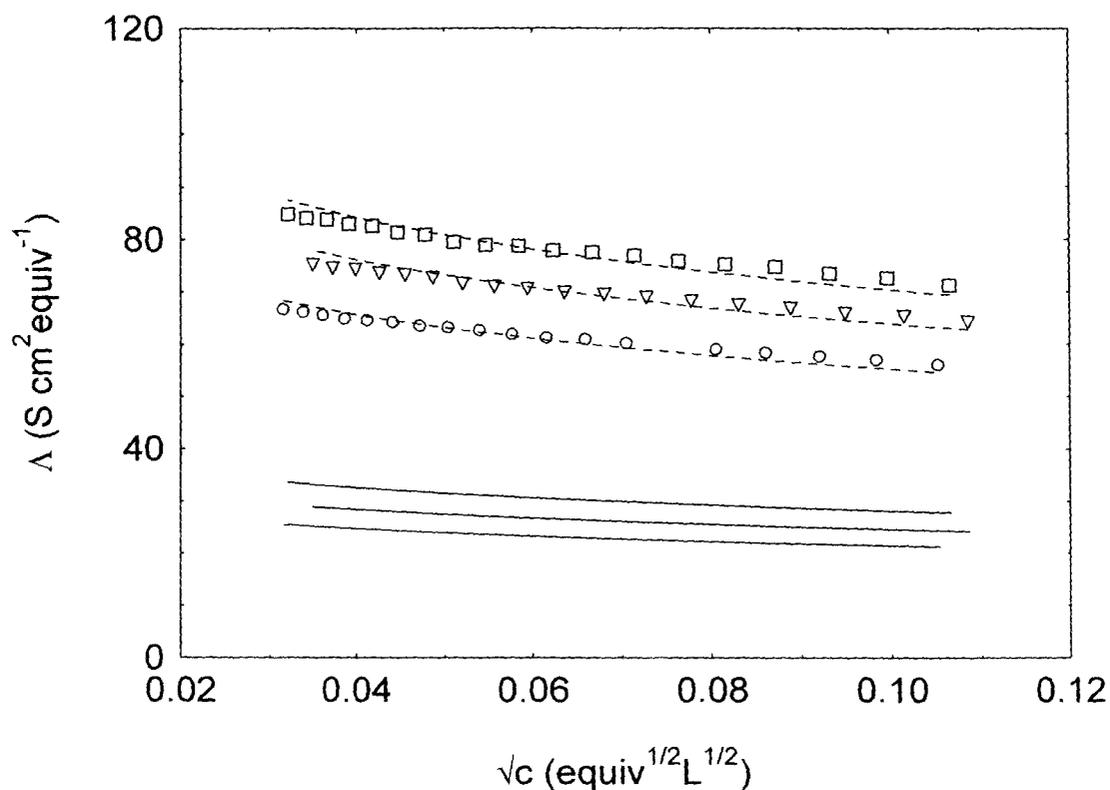
**Table 1.** Charge Density Parameters ( $\xi$ ) Used for the Manning Counterion Condensation Theory and the  $f$  Values for the Best-fit of the Experimental Equivalent Conductances following Scaling Theory Approach for Sodium Polystyrenesulfonate in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

<b>Volume percent of acetonitrile</b>	<b><math>T = 308.15</math> K</b>	<b><math>T = 313.15</math> K</b>	<b><math>T = 318.15</math> K</b>
<b>Manning Charge Density Parameters (<math>\xi</math>)</b>			
20	3.17 (52.00)	3.19 (55.01)	3.22 (59.20)
40	3.58 (40.61)	3.60 (46.43)	3.64 (50.57)
<b>Best-fit <math>f</math> Values (Scaling Theory Approach)</b>			
20	0.368 (1.88)	0.344 (2.09)	0.330 (2.52)
40	0.275 (1.11)	0.267 (1.48)	0.242 (1.70)

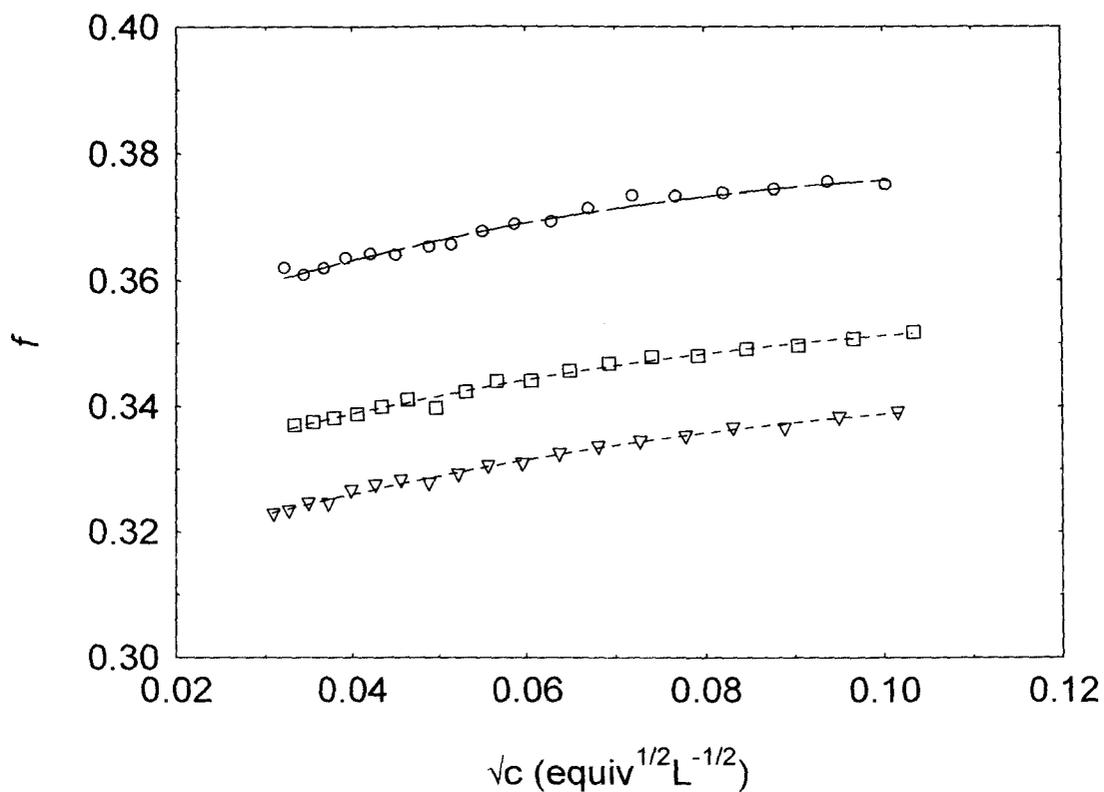
Standard deviations of the fits are given within the parentheses.



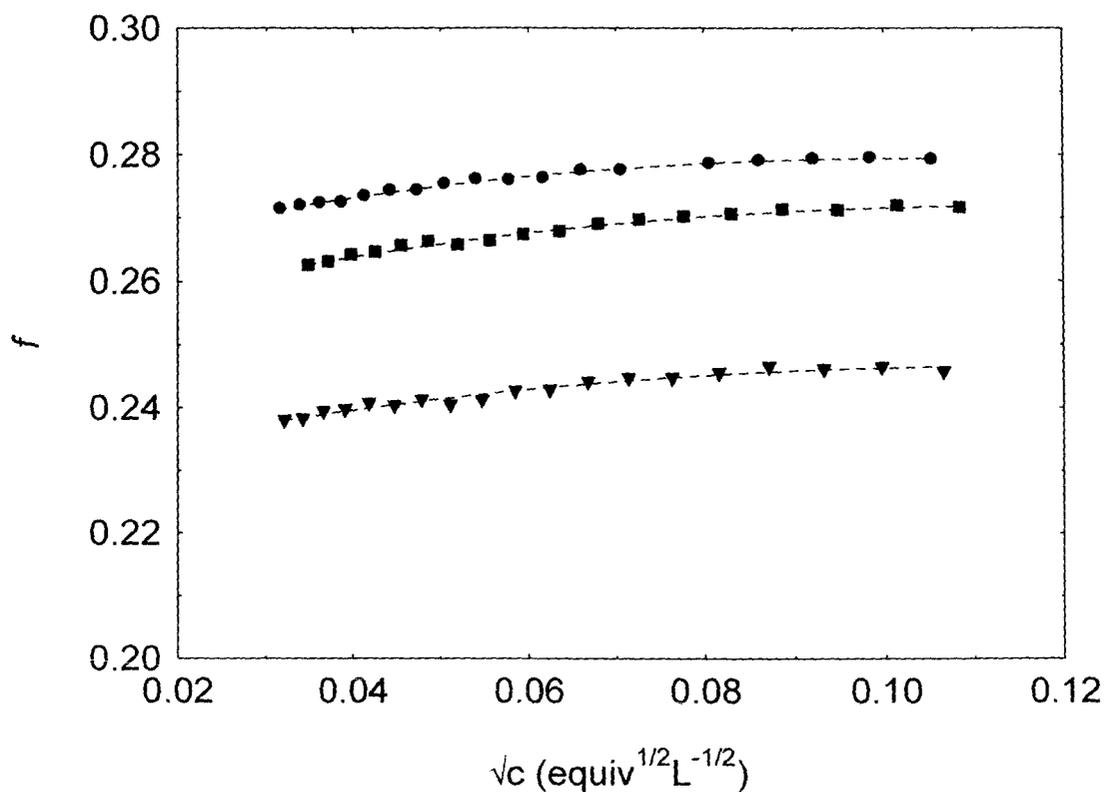
**Figure 1.** Comparison of the experimental values of the equivalent conductivity ( $\Lambda$ ) as a function of the square root of the polyelectrolyte concentration ( $\sqrt{c}$ ) for sodium polystyrenesulfonate in 20 vol percent of acetonitrile in acetonitrile-water mixture with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory. Experimental: 308.15 K ( $\circ$ ), 313.15 K ( $\Delta$ ), and 318.15 K ( $\square$ ). Manning theory: solid lines for 308.15, 313.15, and 318.15 K respectively from bottom to top. Scaling theory: dashed lines.



**Figure 2.** Comparison of the experimental values of the equivalent conductivity ( $\Lambda$ ) as a function of the square root of the polyelectrolyte concentration ( $\sqrt{c}$ ) for sodium polystyrenesulfonate in 40 vol percent of acetonitrile in acetonitrile-water mixture with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory. Experimental: 308.15 K ( $\circ$ ), 313.15 K ( $\Delta$ ), and 318.15 K ( $\square$ ). Manning theory: solid lines for 308.15, 313.15, and 318.15 K respectively from bottom to top. Scaling theory: dashed lines.



**Figure 3.** Fraction of uncondensed counterions ( $f$ ) as a function of the square root of the polyelectrolyte concentration ( $\sqrt{c}$ ) for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media containing 20 vol percent of acetonitrile, calculated using the scaling approach from the conductivity data: 308.15 K (open circles), 313.15 K ( $\square$ ), and 318.15 K (open triangles). The dashed lines are used to guide the eye.



**Figure 4.** Fraction of uncondensed counterions ( $f$ ) as a function of the square root of the polyelectrolyte concentration ( $\sqrt{c}$ ) for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media containing 40 vol percent of acetonitrile, calculated using the scaling approach from the conductivity data: 308.15 K (●), 313.15 K (■), and 318.15 K (▲). The dashed lines are used to guide the eye.

### Effect of Salt on the Conductivity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media

#### Introduction

In Chapter IV, we have reported the results of conductivity measurements on salt-free solutions of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media. Addition of low-molar-mass salts to a polyelectrolyte solution might change its conductivity behavior dramatically and hence studies on the conductivity of polyelectrolytes in presence of a salt might help elucidate the interactions of polyelectrolytes with added salts. In this study, conductivities of NaPSS have been measured in presence of varying concentrations of sodium chloride (NaCl), in acetonitrile-water mixed solvent media as a function of temperature.

Some earlier experimental results<sup>1</sup> on the conductivities of aqueous polyelectrolyte-salt solutions revealed partial agreement with the predictions using the additivity of the specific conductivities of the polyelectrolyte and the salt. The additivity equations were, however, shown<sup>2-5</sup> not to hold for some other aqueous polyelectrolyte-salt systems. It is thus, apparent that in order to arrive at a definite conclusion on the interactions prevailing in polyelectrolyte-salt solutions from the results of conductivity measurements, more investigation is needed considering as many parameters as possible.

We, therefore, obtained accurate conductivity data for the polyelectrolyte-salt system mentioned above. The present study considers a multitude of parameters such as relative permittivity of solvent, concentration of polyelectrolyte, concentration of added salt and the temperature.

These experimental results have been analyzed to evaluate the extent of deviation from the additivity in order to assess the polyelectrolyte-salt interactions with a view to obtain information on the changes in the polyion conformation if any induced by the salt.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. Triply distilled water with a specific conductance of less than  $10^{-6}$  S cm<sup>-1</sup> at 308.15K was used for the preparation for the solvent mixtures. The physical properties of acetonitrile-water mixture used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1 of Chapter III.

Also included in this table are the limiting equivalent conductivities of the counterion (Na<sup>+</sup>),  $\lambda_c^0$ , in 10, 20, and 40 volume percent of acetonitrile-water mixtures taken from our earlier investigation<sup>6</sup> (*cf.* Appendix).

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was 70 kDa.

Conductance measurements were performed on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm<sup>-1</sup> and having an uncertainty of 0.01%. The measurements were made in a water bath maintained within  $\pm 0.005$  K of the desired temperature. The details of the experimental procedure have been described earlier.<sup>7</sup> Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

In order to avoid moisture pickup, the experimental solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates and the results were averaged.

## Results and Discussion

### *Primitive Additivity*

First, the experimental specific conductivity data were analyzed phenomenologically in terms of an additivity contributions of the polyelectrolyte and the simple salt to the total specific conductivity (known as “primitive” additivity). Such an approach is usually used in the literature in describing the behaviour of salt-containing polyelectrolyte solutions.<sup>2-4</sup> Traditionally, this approach takes the form of an assumed additivity of the specific

conductances of the polyelectrolyte and of the salt, which gives the specific conductance ( $\kappa$ ) of the polyelectrolyte in a salt solution through the following equation,

$$\kappa = \kappa_p + \kappa_s \quad (1)$$

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

$$\kappa_p = \kappa - \kappa_s \quad (2)$$

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 in the present study. This is clearly evident from Figures 1a, 2a, 3a, 4a, 5a, 6a, 7a, 8a, and 9a where experimental values of specific conductivities ( $\kappa$ ) of sodium polystyrenesulfonate in presence of varying concentrations of sodium chloride in acetonitrile-water mixtures have been plotted as a function of the equivalent polyelectrolyte concentration ( $c$ ).

The fact that the true value of the polyelectrolyte specific conductance cannot be calculated from the specific conductance data obtained in salt-containing polyelectrolyte solutions by using simple additivity of polyelectrolyte and simple salt specific conductances demonstrates clearly the existence of polyelectrolyte-salt interactions. This kind of behaviour of polyelectrolyte-salt solutions has also been reported earlier for other systems.<sup>3-6</sup>

### ***Modified Additivity***

Later Ander group<sup>2,3</sup> modified the “primitive” additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution through

$$\kappa_p = \kappa - \kappa_s \left( D_2 / D_2^0 \right) \quad (3)$$

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 interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be  $\kappa_s(D_2 / D_2^0)$ .

Now, in absence of the experimental data for  $D_2 / D_2^0$  for the present system, these were calculated by using the Manning's theory as<sup>11</sup>

$$D_2 / D_2^0 = 1 - (1/3)\xi X [2 + X(1 + \pi\xi^{-1})]^{-1} \quad (4)$$

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

$$D_2 / D_2^0 = 1 - (1/3)\xi^{-1} X [\xi^{-1} X(1 + \pi) + 2]^{-1} \quad (5)$$

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

Figures 1b, 2b, 3b, 4b, 5b, 6b, 8b, and 9b clearly show that the "modified" additivity also fails to provide the true values of the polyelectrolyte specific conductance from the specific conductance data obtained in salt-containing polyelectrolyte and simple salt solutions. Therefore, the effects of salt on the specific conductance for the system under investigation could not be quantitatively described by the additivity inspite of taking into account the interactions among all ionic species present in solution following Eq. (3).

## Conclusions

The electrical conductances of solutions of sodium polystyrenesulfonate in three acetonitrile-water mixed solvent media containing 10, 20, and 40 volume percent acetonitrile have been measured at three different temperatures namely, 308.15, 313.15, and 318.15 K in presence of sodium chloride. The conductance data have been analyzed on the basis of so-called "primitive" and "modified" additivities of the specific conductances of the polyelectrolyte and salt. Although the performance of the "modified" additivity is somewhat better than the "primitive" one, both fail to provide a quantitative description of the experimental conductivity of sodium polystyrenesulfonate-sodium chloride system in acetonitrile-water mixtures.

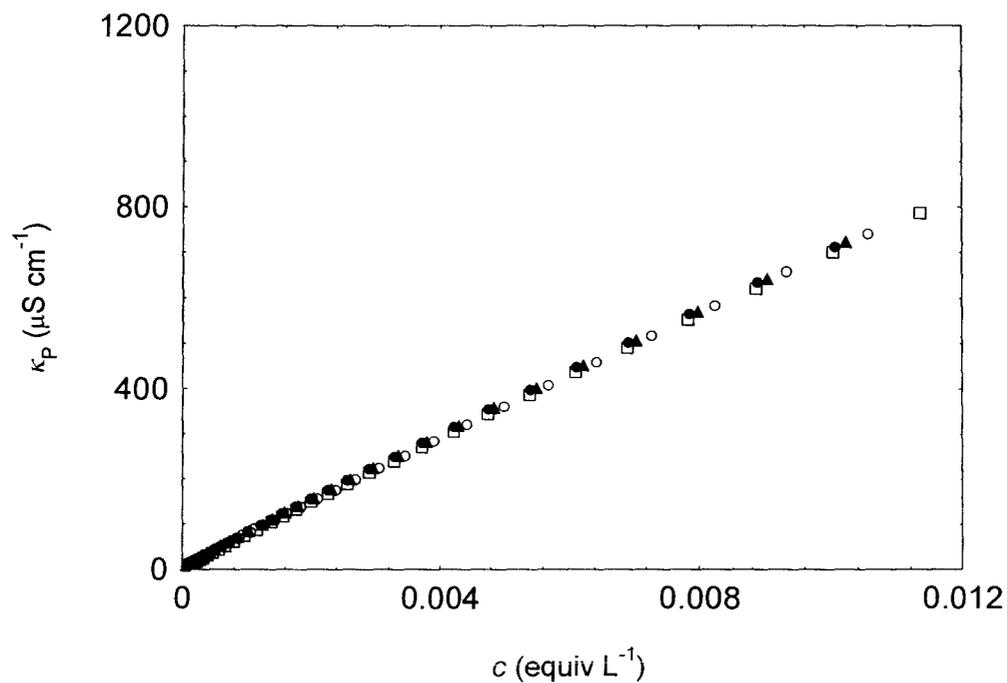
The observations indicate that

- (1) 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. (4) and (5), might play a decisive role,
- (2) the polyion specific conductance is greatly affected by the addition of the salts. In the present case, the polyion mobility should decrease with the addition of salts, suggesting the decrease in the apparent charge of the polyion due to its changing conformation in salt solutions,
- (3) 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, and
- (4) the polyion mobility is sensitive to the concentration of the added salt which might induce some conformational changes in the polyion structure thus affecting its specific conductance in salt solutions. The effect is found to be more prominent as the concentration of the added salt is increased.

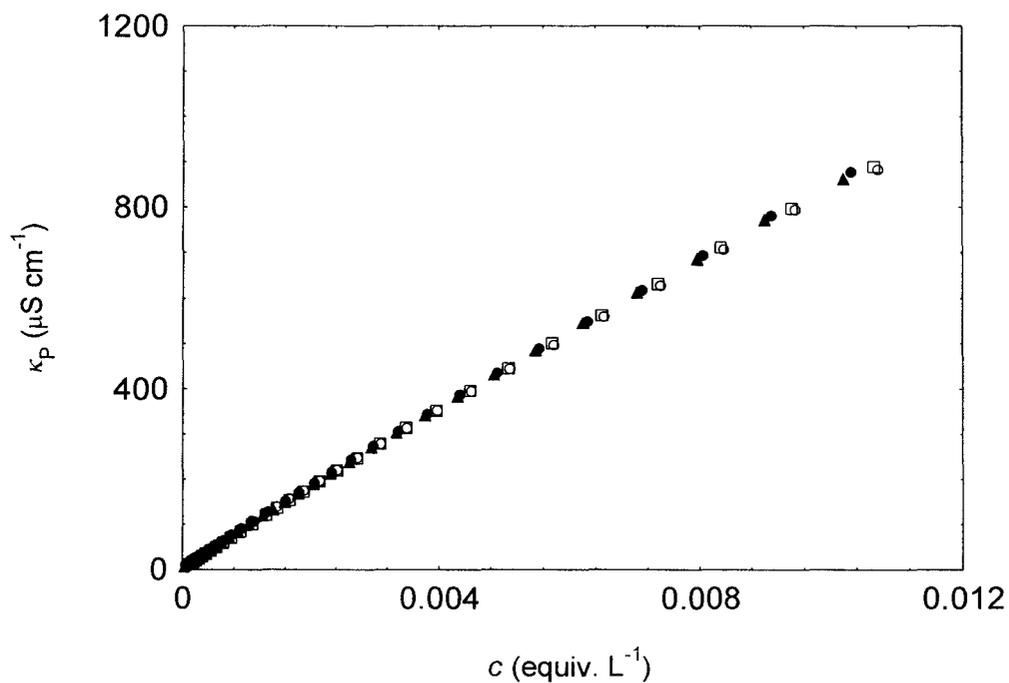
Finally, it can be concluded that the theory of the conductivity of polyelectrolyte-salt solutions is still not completely developed to elucidate the interactions in such systems and that it needs modifications on the lines described above.

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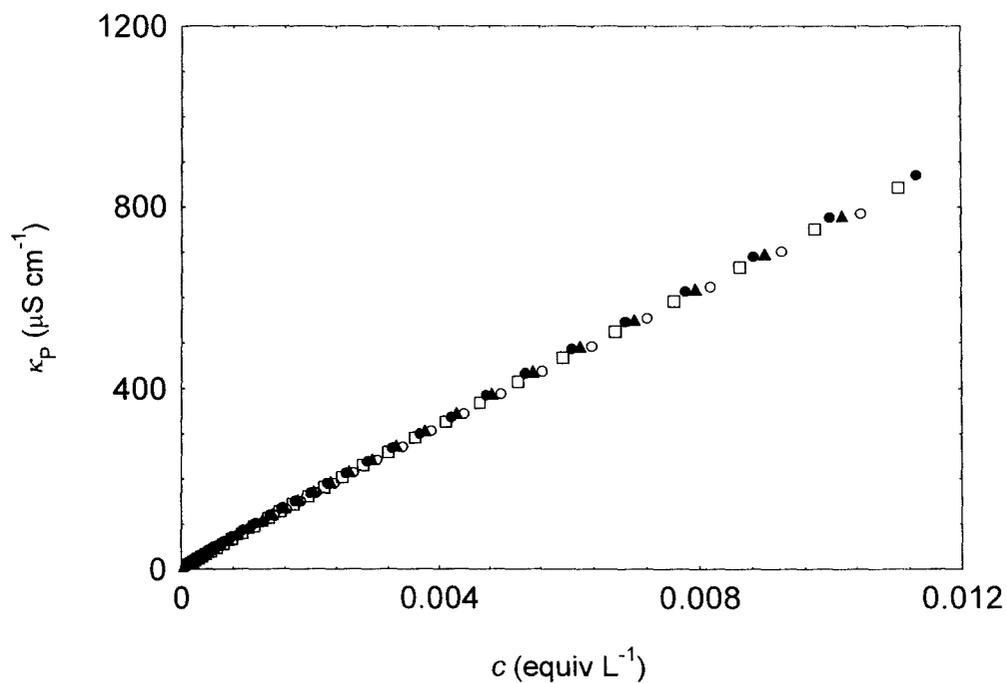
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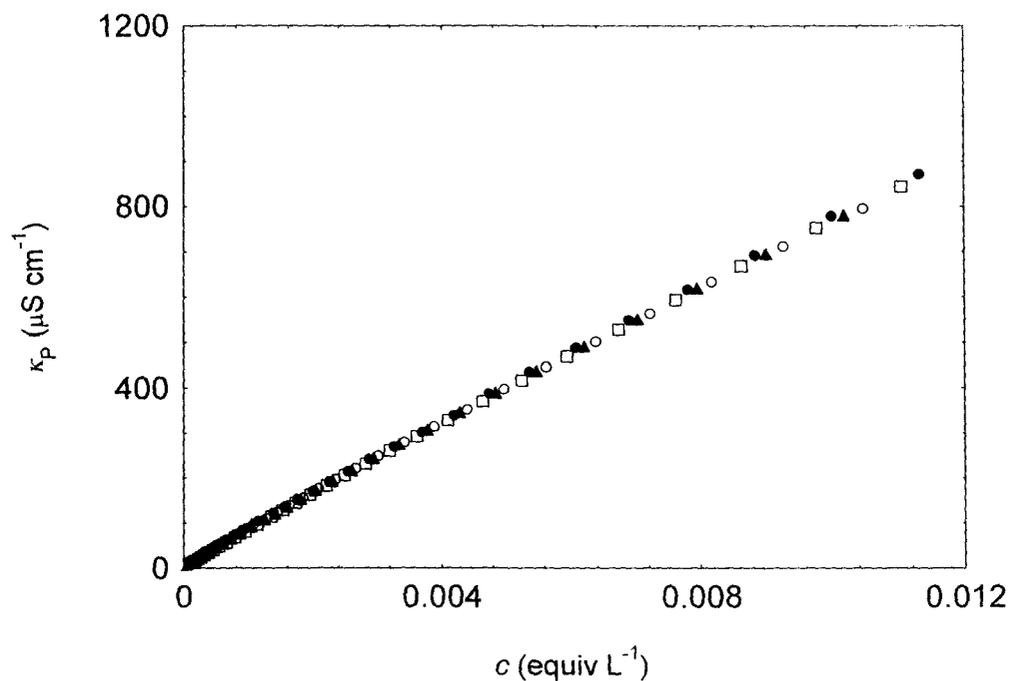
**Figure 1a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



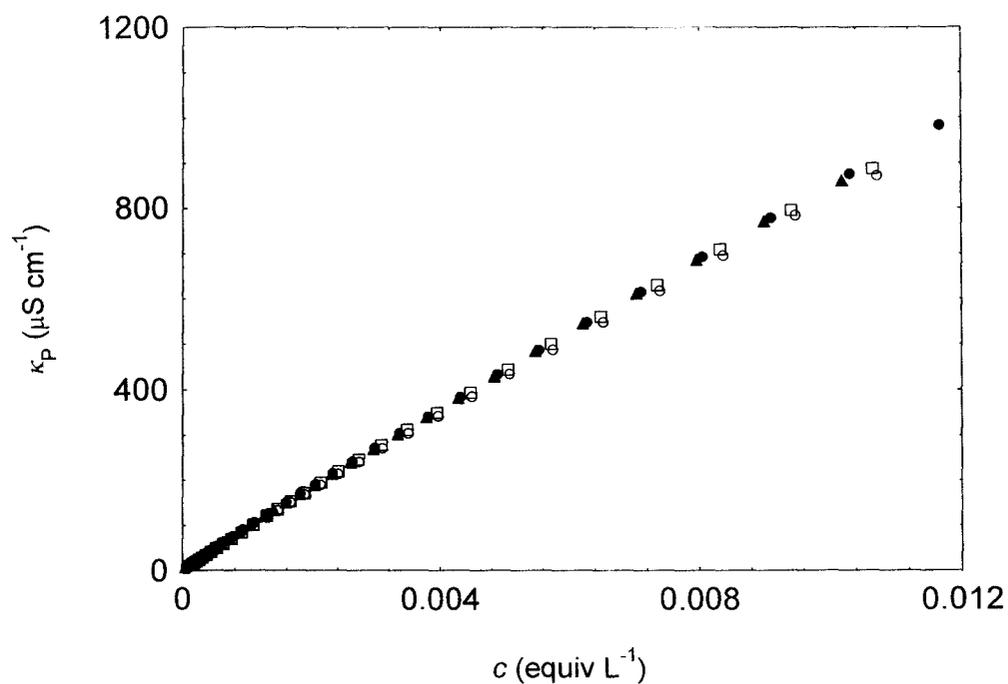
**Figure 1b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



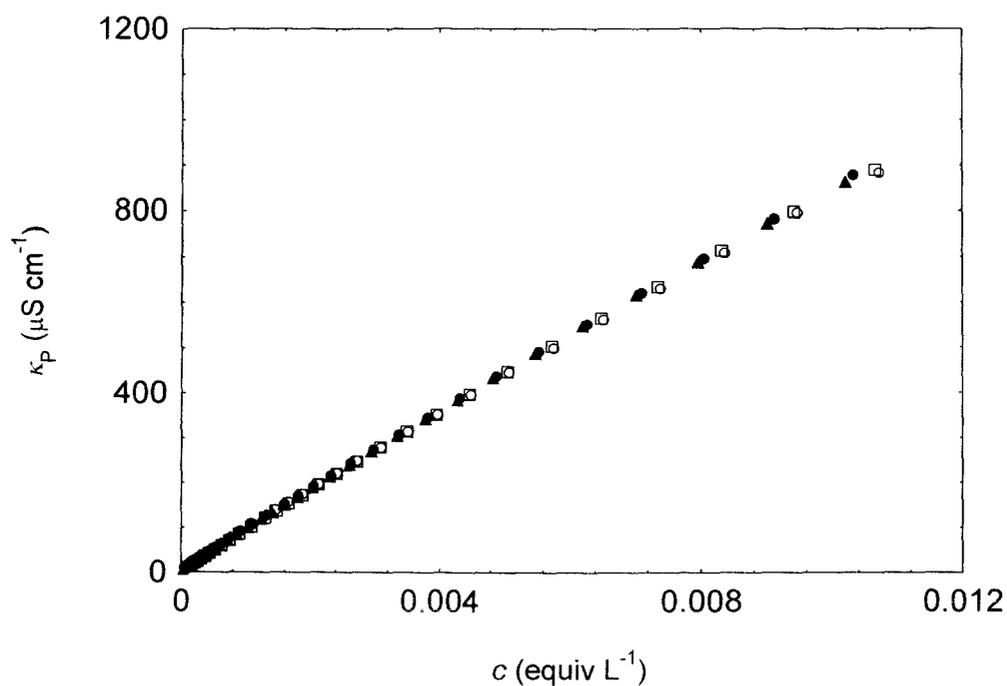
**Figure 2a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



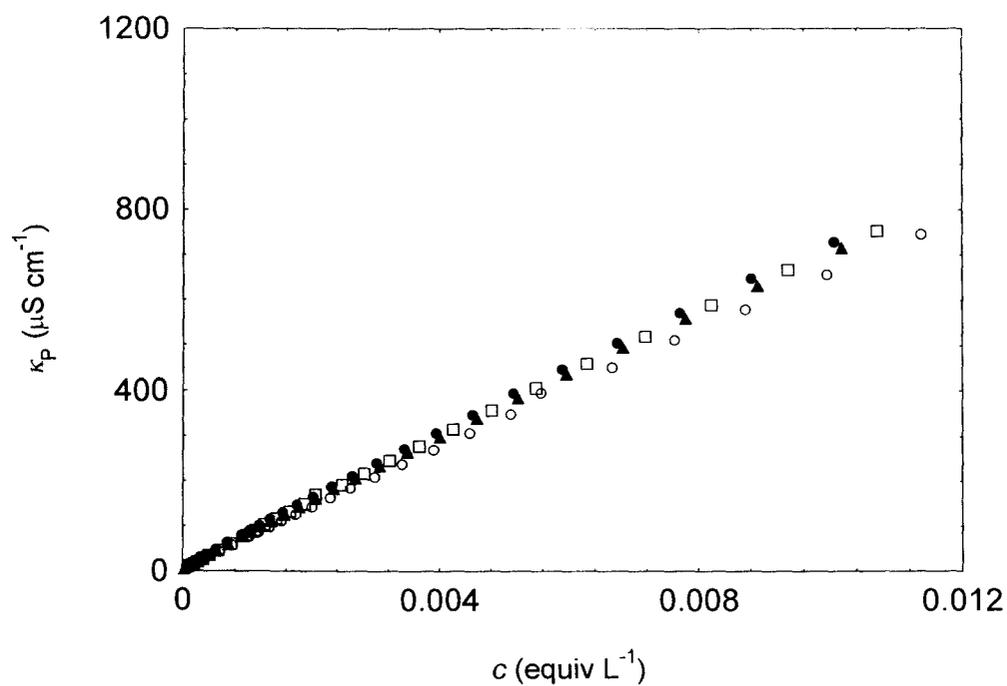
**Figure 2b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): ( $\bullet$ ); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl ( $\blacktriangle$ ),  $0.0001 \text{ mol L}^{-1}$  NaCl ( $\square$ ), and  $0.001 \text{ mol L}^{-1}$  NaCl ( $\circ$ ).



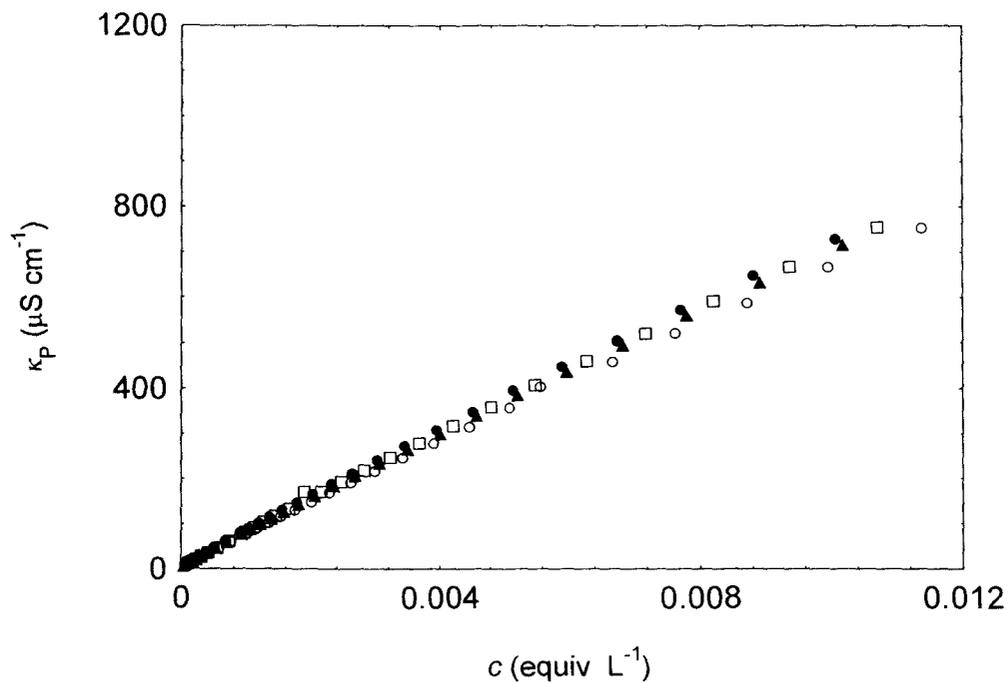
**Figure 3a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



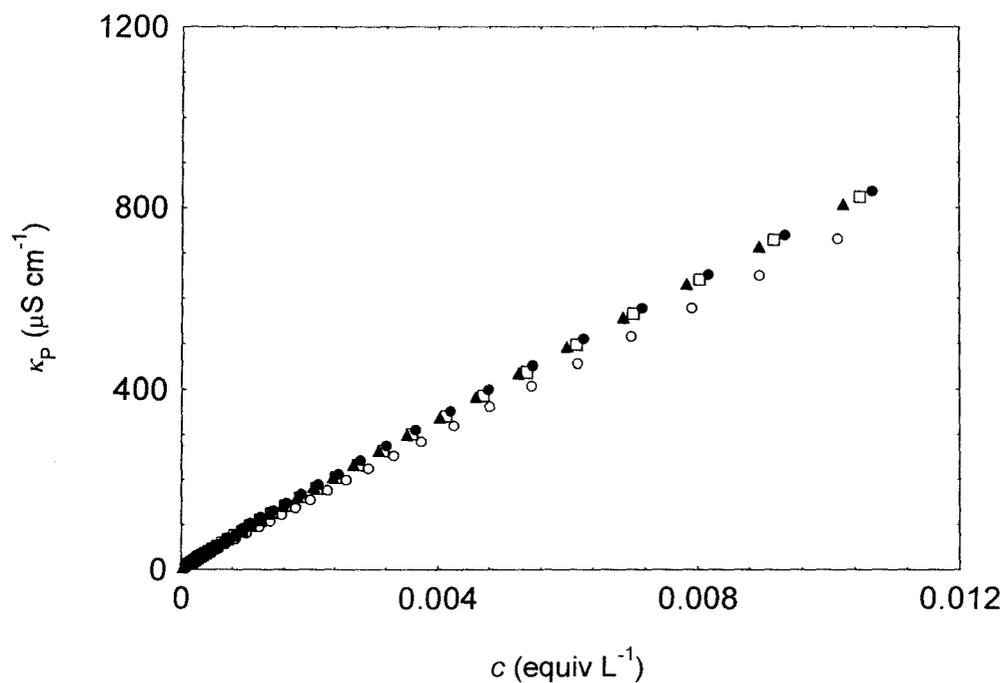
**Figure 3b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Symbols represent modified additivity. (▲) 0.00001, (□) 0.0001, and (○) 0.001 mol L<sup>-1</sup> NaCl respectively.



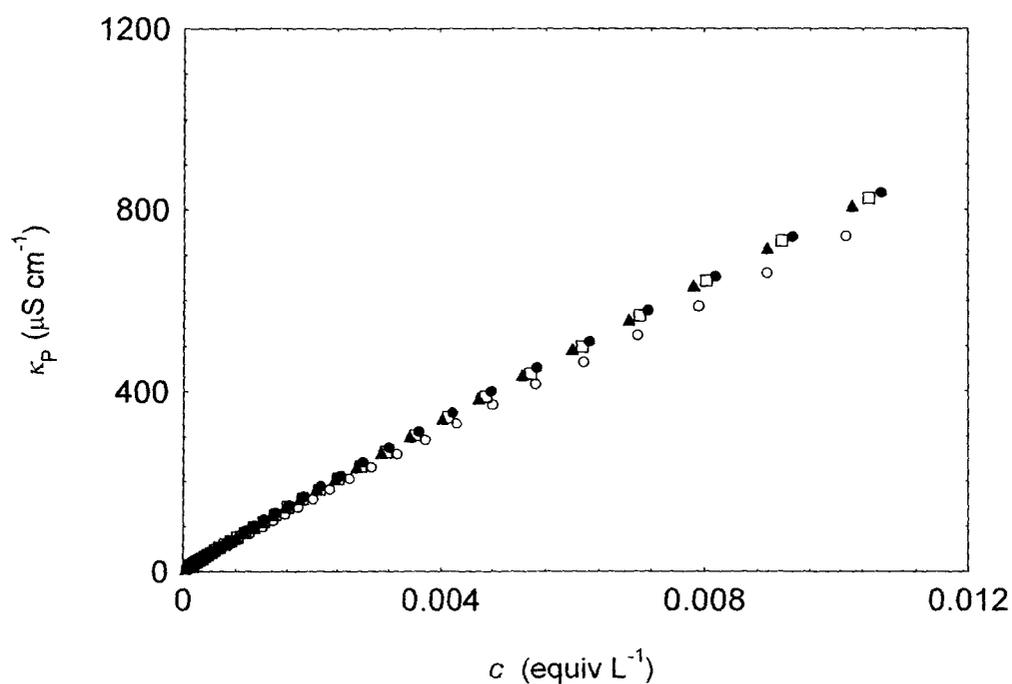
**Figure 4a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



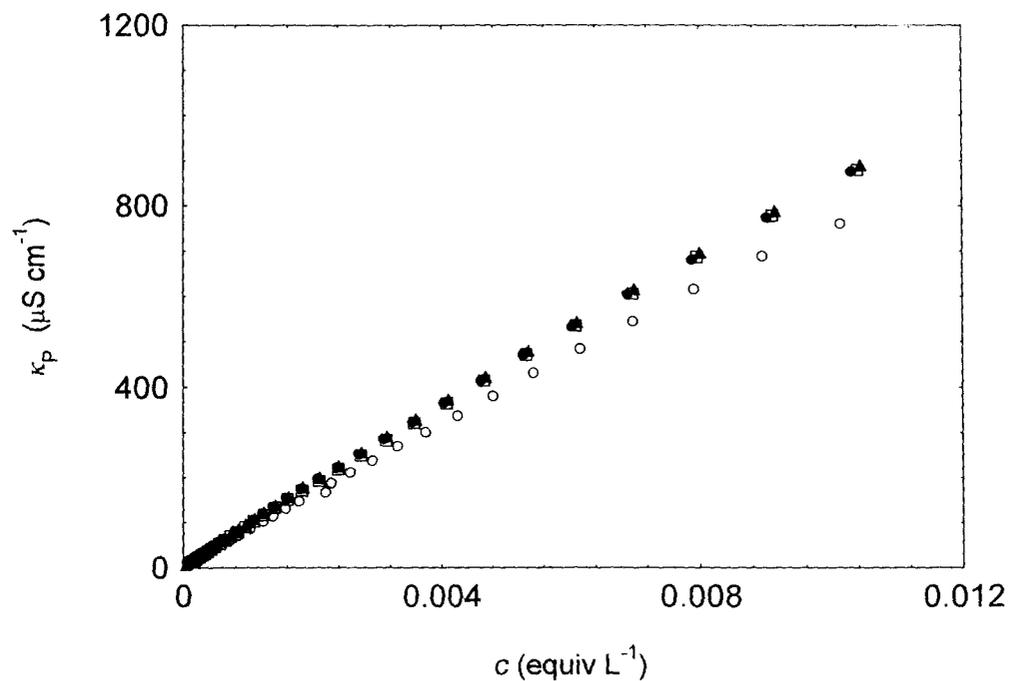
**Figure 4b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



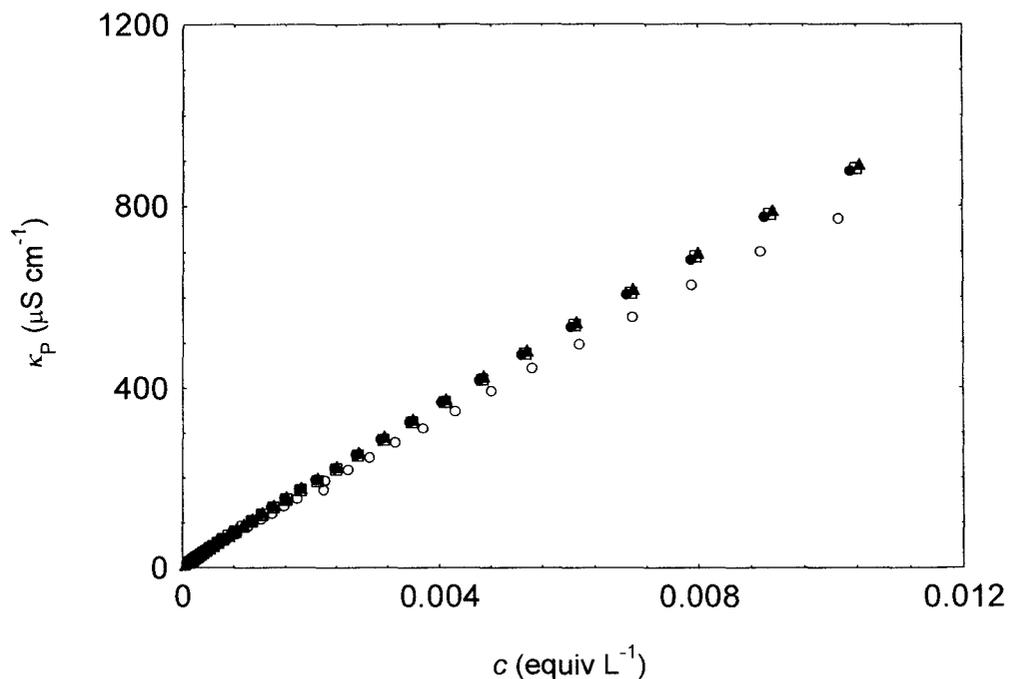
**Figure 5a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L<sup>-1</sup> NaCl (▲), 0.0001 mol L<sup>-1</sup> NaCl (□), and 0.001 mol L<sup>-1</sup> NaCl (○).



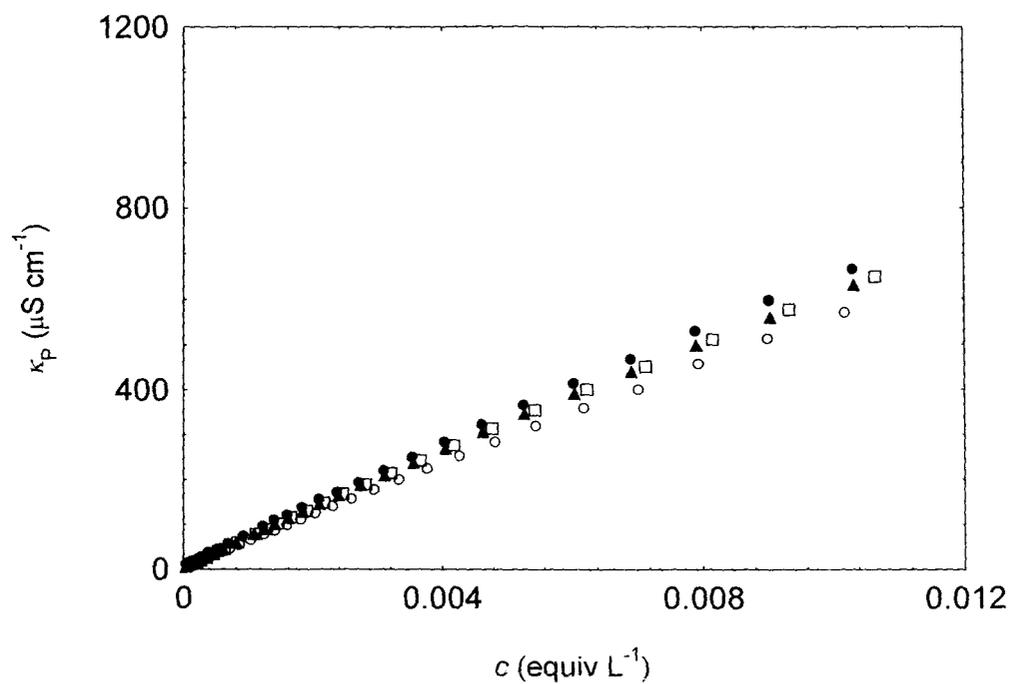
**Figure 5b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



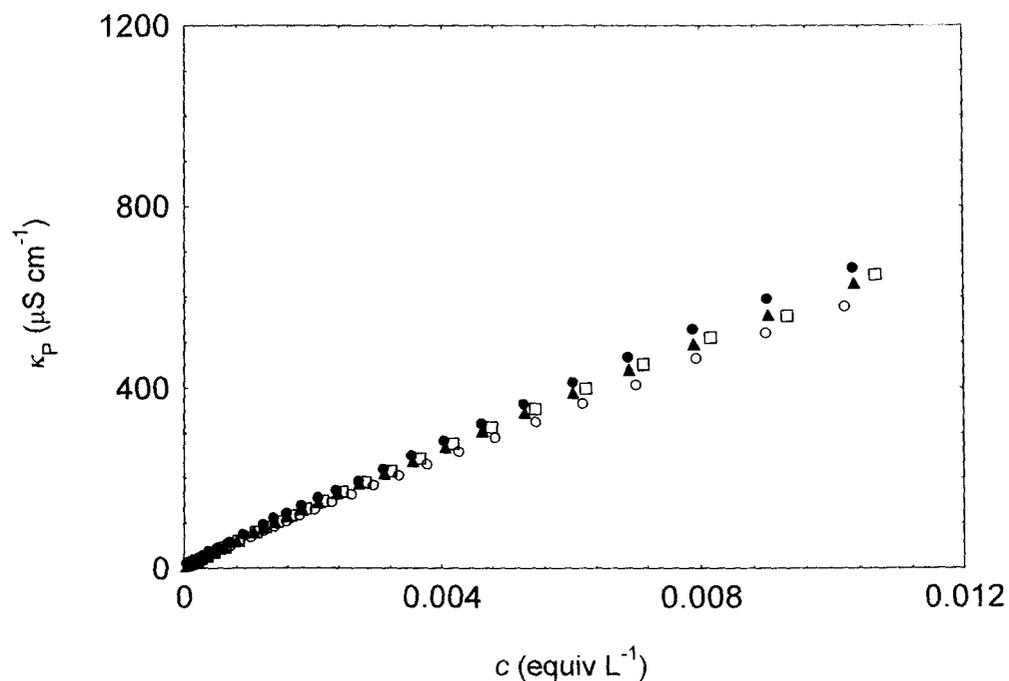
**Figure 6a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



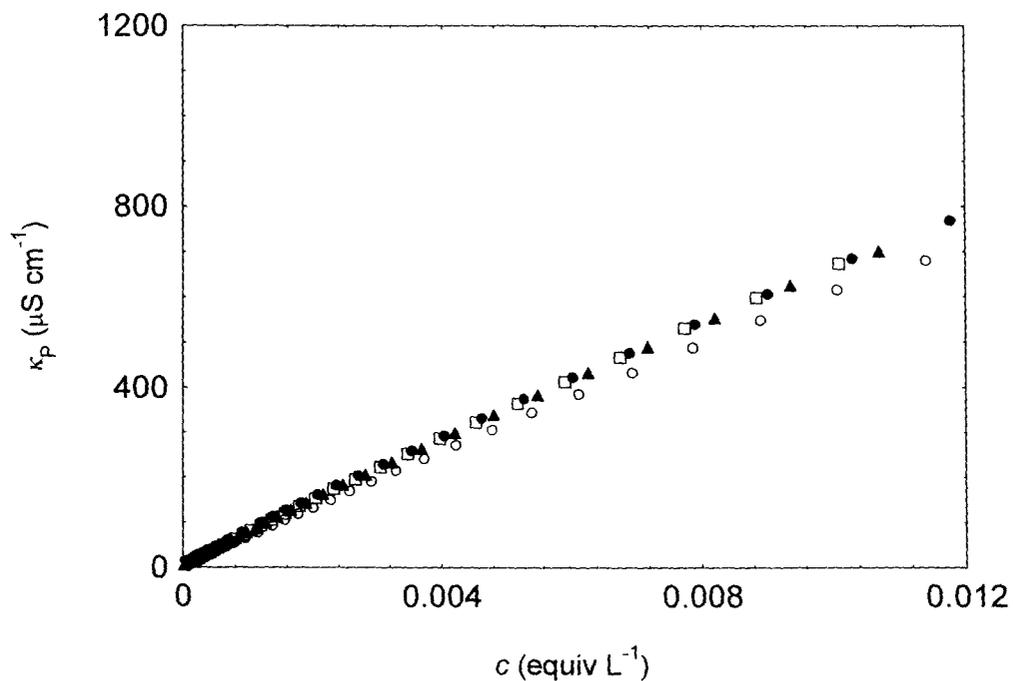
**Figure 6b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



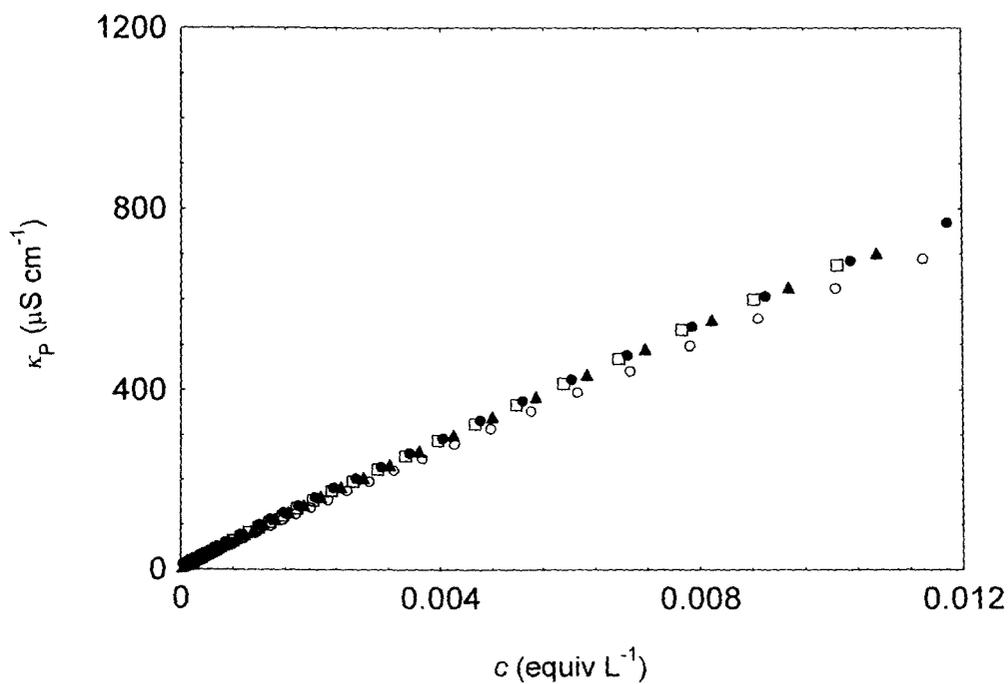
**Figure 7a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): ( $\bullet$ ); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl ( $\blacktriangle$ ),  $0.0001 \text{ mol L}^{-1}$  NaCl ( $\square$ ), and  $0.001 \text{ mol L}^{-1}$  NaCl ( $\circ$ ).



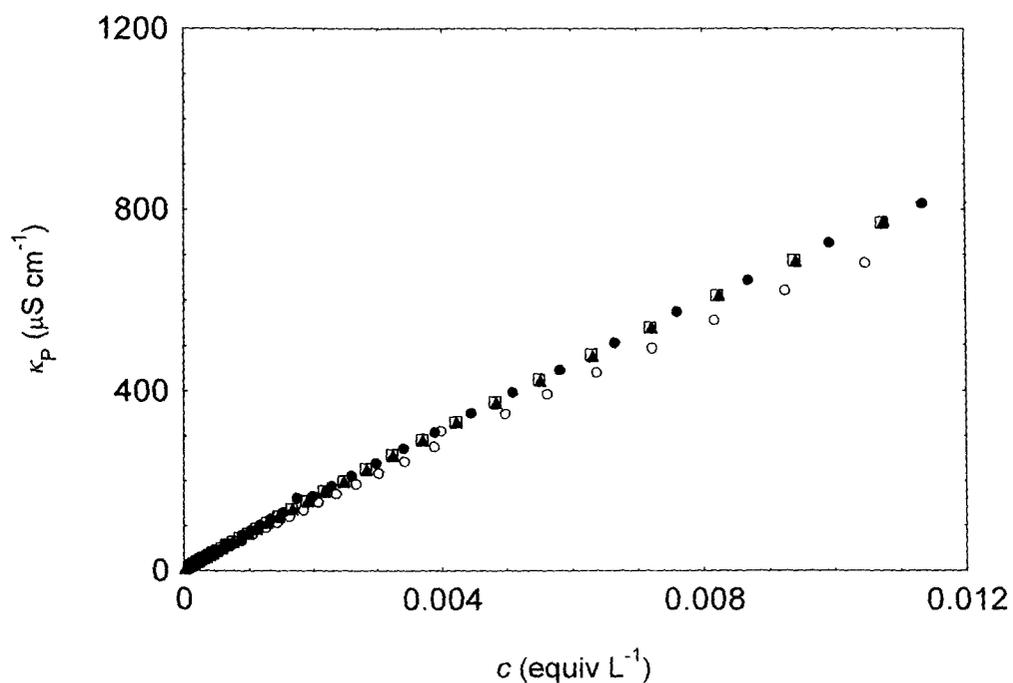
**Figure 7b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 308.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



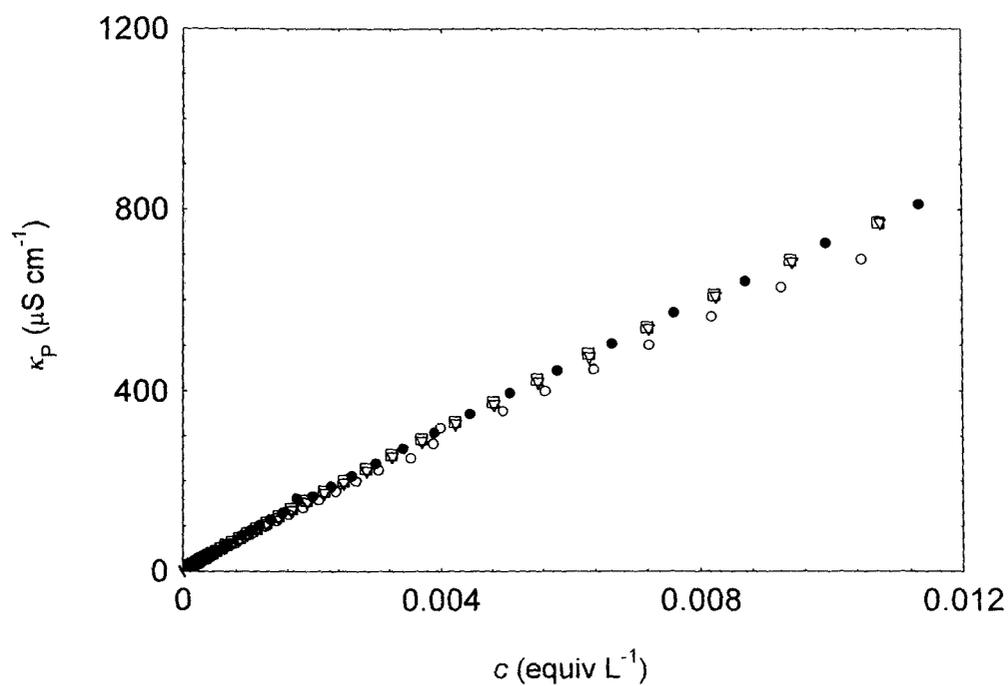
**Figure 8a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



**Figure 8b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 313.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



**Figure 9a.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl (▲),  $0.0001 \text{ mol L}^{-1}$  NaCl (□), and  $0.001 \text{ mol L}^{-1}$  NaCl (○).



**Figure 9b.** Specific conductivities of NaPSS as a function of the polymer concentration ( $c$ ) at 318.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): ( $\bullet$ ); Results according to modified additivity, in presence of  $0.00001 \text{ mol L}^{-1}$  NaCl ( $\blacktriangle$ ),  $0.0001 \text{ mol L}^{-1}$  NaCl ( $\square$ ), and  $0.001 \text{ mol L}^{-1}$  NaCl ( $\circ$ ).

## Intrinsic Viscosities of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media Using the Isoionic Dilution Method

### Introduction

In discussing the conformation of a single polymer chain from viscometric data, information about the intrinsic viscosity  $[\eta]$  is indispensable. Because of the presence of electric charges along the polymer chains in polyelectrolytes, the behavior of these species in solutions is entirely different from that of the uncharged (neutral) polymers and these are characterized by complex interactions, conformations, structures and dynamics.<sup>1-4</sup> It is thus not surprising that although the experimental determination of the intrinsic viscosity  $[\eta]$  of uncharged polymers is rather straightforward, that of salt-free polyelectrolyte solutions or of polyelectrolyte solutions with small amount of added salts presents a great challenge.

In case of uncharged polymer solutions, the reduced viscosity ( $\eta_{sp}/c$ ;  $\eta_{sp}$  = specific viscosity and  $c$  = polymer concentration) varies linearly with concentration  $c$  in dilute solutions which led Huggins to propose the following equation<sup>2,5</sup>

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity describing the solvodynamic behavior of the polymer molecules in solution and  $k_H$  is the Huggins constant which is a characteristic for a given polymer-solvent system. This well-known relation has been extensively used for determining the intrinsic viscosity of uncharged polymers simply by extrapolating  $\eta_{sp}/c$  vs.  $c$  values to  $c = 0$ . On the other hand, the reduced viscosity of salt-free polyelectrolyte solutions exhibits an anomalous behavior.

Early investigations appeared to suggest a monotonous increase in the reduced viscosity of polyelectrolyte solutions with no-added salt as one lowers the polyion concentration.<sup>6,7</sup> In these studies, which are summarized in the pioneering work of Fuoss,<sup>6,7</sup> a straight line is obtained when the reciprocal of reduced viscosity is plotted as a function of the square root of the polyelectrolyte concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the reciprocal intrinsic viscosity. However, careful investigations on the

dilute solution behavior revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum, and normal polymer behavior is recovered as the polyelectrolyte concentration approaches zero. Thus, the method of Fuoss could not be employed to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. It has been argued that the maximum in the  $\eta_{sp}/c$  vs.  $c$  profiles results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum, the pair potential attains its maximum value – it decreases upon dilution because of an increase in intermolecular distances and it also decreases with increasing concentration due to the screening of electrostatic interactions. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polyelectrolyte concentration and, therefore, was close to the limit of the accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations below the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

Isoionic dilution<sup>8,9</sup> is the most straightforward method for the determination of the intrinsic viscosity of a polyelectrolyte in solution. In accordance with 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 of the salt solution, 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 circumstances 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.

Despite the success of this method for the determination of intrinsic viscosity of polyelectrolytes in solution in a convenient manner, very little attention has been paid in this direction.<sup>8-12</sup>

The principal objective of the present contribution is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media. The influences of the medium, total ionic strength, and temperature on the counterion condensation behavior and on the changes in the conformation, if any, of the polyion will also be investigated.

## Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of  $0.76570 \text{ g.cm}^{-3}$  and a co-efficient of viscosity of  $0.3126 \text{ mPa.s}$  at  $308.15 \text{ K}$ ; these values are in good agreement with the literature values.<sup>13</sup> Triply distilled water with a specific conductance of less than  $10^{-6} \text{ S.cm}^{-1}$  at  $308.15 \text{ K}$  was used for the preparation of the mixed solvents.

NaPSS used in these investigations was purchased from Aldrich Chemical. The average molecular weight ( $M_w$ ) of the sample was  $70,000$  with a degree of substitution (DS) of  $1$ , and these values agree well with those obtained from physiochemical characterization in the present study.

The viscometric measurements were performed at  $298.15$ ,  $308.15$ , and  $318.15 \text{ K}$  using a Schultz-Immergut-type viscometer<sup>14</sup> with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within  $\pm 0.005 \text{ K}$  of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.<sup>15,16</sup> Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated, measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

The reduced viscosity is obtained from

$$\frac{\eta_{sp}}{c} = \frac{t - t_0}{t_0} \frac{1}{c} \quad (2)$$

where  $t$  and  $t_0$  are the measured flow times of the polyelectrolyte solution and of the pure solvent, respectively.

To avoid moisture pick up, all of the solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

## Results and Discussion

The typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free sodium polystyrenesulfonate solution in acetonitrile-water mixtures with 10, 20, and 40 vol% of acetonitrile at 298.15, 308.15, and 318.15 K are shown, respectively, in Figures 1 to 9. In absence of an added salt, the reduced viscosity is found to increase as the polyelectrolyte concentration decreases, for all systems investigated, bending up at low concentrations thus manifesting the typical polyelectrolyte behavior. No maximum was, however, detected in the  $\eta_{sp}/c$  versus  $c$  profiles within the concentration range studied here.

Isoionic dilution was proposed to avoid the conformational change of the polyion thus eliminating the anomalous polyelectrolyte behavior and to determine the intrinsic viscosity of solution.<sup>8-12</sup> As we know that the intrinsic viscosity is the parameter which enables characterization of dimension and configuration of polymer, this may play a crucial role in the discussion of polyelectrolyte behavior in dilute solutions.

Isoionic dilution of sodium polystyrenesulfonate solutions have been performed at two different total ionic strengths (at polyelectrolyte concentrations of 0.0065 and 0.0125 equiv L<sup>-1</sup>) in acetonitrile-water mixtures containing 10, 20 and 40 vol % of acetonitrile at 298.15, 308.15, and 318.15 K using sodium chloride as the added salt. Figures 1-9 also include the experimental data for the isoionic dilutions.

The reduced viscosity data as functions of polyelectrolyte concentration resulting from the isoionic dilution can be described by the well-known Huggins equation,<sup>2,5</sup> Eq. (1).

From the present experimental  $\eta_{sp}/c$  versus  $c$  data, the intrinsic viscosities and the Huggins constants have been determined by the method of least-squares using Eq. (1) and these are displayed in Figures 10 - 13.

## ***Influence of Total Ionic Strength, Medium and Temperature on the Intrinsic Viscosities and the Huggins Constants***

The intrinsic viscosities and the Huggins constants for the present polyelectrolyte system vary with the total ionic strength, the medium, and the experimental temperature (*cf.* Table 1 and Figures 10-13). This observation, thus, indicates that the polyelectrolyte NaPSS differs quite appreciably in its solvodynamic and thermodynamic behaviours under varying experimental conditions.<sup>17,18</sup>

The temperature dependence of the Huggins constant values can be conveniently described by the following equation:

$$k_H = Ae^{-B/T} \quad (3)$$

The values of the constants  $A$  and  $B$ , obtained by the method of least-squares analysis, along with the correlation coefficients of fits (as  $r^2$ ) are listed in Table 2.

### ***Influence of Medium***

At 298.15, 308.15 and 318.15 K, and at a given value of the total ionic strength, the intrinsic viscosities are found to decrease as the medium becomes richer in acetonitrile (Table 1 and Figure 10). Moreover, the Huggins constants are found to increase with increasing amount of acetonitrile in the mixed solvent media (Table 1 and Figure 11). It is thus apparent that the polyion chain swells differently in different solvents and it would be interesting to relate the intrinsic viscosities to the parameters of thermodynamic affinity of a solvent for a polymer as described by Alfrey *et. al.*<sup>17,18</sup> The above observation demonstrates that the solvent interacts poorly with the polymer (*i.e.*, with less thermodynamic affinity) as the medium gets richer in acetonitrile and hence the polymer-polymer contacts are becoming more probable than the polymer-solvent contacts, and therefore the solvodynamic dimension of the chain will be gradually reduced. This explains both the lower intrinsic viscosity and the higher values of the Huggins constants in a solvent richer in acetonitrile. This is consistent with the general view that high  $k_H$  values are the characteristics of the poor solvents.

### ***Influence of Ionic Strength***

The intrinsic viscosities are found to decrease as the total ionic strength of the solution increases as reported in Table 1 at a particular solvent composition and at a particular

temperature. Counterion binding onto the polyion chain is considerably enhanced, as the concentration of the ions in the solution increases. This causes more effective screening of the chain charges in high ionic strength solution, decreasing the intramacromolecular electrostatic repulsions (and hence decreasing  $k_H$ , *cf.* Table 1) and resulting in partial coiling of the macromolecules, and hence, in a decrease in the intrinsic viscosity of the solution.

### ***Influence of Temperature***

Intrinsic viscosity values are found to increase regularly with temperature a given solvent medium when the total ionic strength is maintained at a constant level (Table 1, and Figure 12). The Huggins constant, on the other hand, decreases with temperature in these cases (Table 1, and Figure 13). This is directly connected to the temperature coefficient of the second Virial coefficient ( $A_2$ ). The present observation points to the fact that the thermodynamic affinity of the solvent for the polymer (*i.e.*, the polymer-solvent interaction) improves as the temperature rises (*i.e.*,  $A_2$  increases) in a given solvent, and hence the chain expands more resulting in an increase in the intrinsic viscosity values with an elevation of temperature. Increase in the polymer-solvent interaction results in a decrease in the polymer-polymer interaction,<sup>19</sup> manifested by the decreasing Huggins constant values as a function temperature. Studies on the temperature dependence of Huggins constants for polyelectrolytes are, to the best of our knowledge, not available in the literature. However,  $k_H$  values reported<sup>18</sup> for a polystyrene sample are found to decrease with the increase in temperature as observed in the present work.

### **Conclusions**

The present chapter reported precise measurements on the viscosities of the solutions of an anionic polyelectrolyte sodium polystyrenesulfonate in acetonitrile–water mixed solvent media containing 10, 20, and 40 vol percent of acetonitrile at 298.15, 308.15, and 318.15 K. The intrinsic viscosities and the Huggins constants of the polyelectrolyte solutions were obtained using the Huggins equation through isoionic dilution whereby maintaining the total ionic strengths at polyelectrolyte concentrations of 0.0065, and 0.0125 equiv L<sup>-1</sup> with sodium chloride. The influences of medium and the total ionic strength on the intrinsic viscosities have been interpreted in terms of counterion condensation and coiling behaviour in the investigated solutions. The variations of Huggins constants, on the other hand, provided information on the intermolecular interactions.

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**Table 1.** Intrinsic viscosities  $[\eta]$ , Huggins Constants  $k_H$ , and Correlation Coefficient of Fits (as  $r^2$ ) of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixtures Aontaining 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15 and 318.15 K

Vol Percent of acetonitrile in acetonitrile –water mixed media	Polyelectrolyte concentration where isoionic dilutions were performed (equiv L <sup>-1</sup> )	$[\eta]$ (L equiv <sup>-1</sup> )	$k_H$	$r^2$
<b><i>T</i> = 298.15 K</b>				
10	0.0065	11.60 ± 0.09	9.88 ± 0.14	0.9991
10	0.0125	9.43 ± 0.19	6.62 ± 0.26	0.9954
<b><i>T</i> = 308.15 K</b>				
10	0.0065	12.27 ± 0.22	7.44 ± 0.30	0.9934
10	0.0125	10.06 ± 0.12	4.83 ± 0.13	0.9976
<b><i>T</i> = 318.15 K</b>				
10	0.0065	13.05 ± 0.22	5.17 ± 0.29	0.9903
10	0.0125	10.68 ± 0.17	3.27 ± 0.18	0.9881
<b><i>T</i> = 298.15 K</b>				
20	0.0065	9.51 ± 0.13	14.48 ± 0.32	0.9980
20	0.0125	7.75 ± 0.17	10.39 ± 0.33	0.9960
<b><i>T</i> = 308.15 K</b>				
20	0.0065	10.45 ± 0.20	10.34 ± 0.43	0.9930
20	0.0125	8.41 ± 0.18	7.82 ± 0.31	0.9937
<b><i>T</i> = 318.15 K</b>				
20	0.0065	11.16 ± 0.11	8.02 ± 0.20	0.9976
20	0.0125	9.12 ± 0.14	5.80 ± 0.21	0.9949
<b><i>T</i> = 298.15 K</b>				
40	0.0065	8.63 ± 0.23	17.95 ± 0.68	0.9942
40	0.0125	6.46 ± 0.18	16.56 ± 0.53	0.9958

Table 1. continued

Table 1. continued

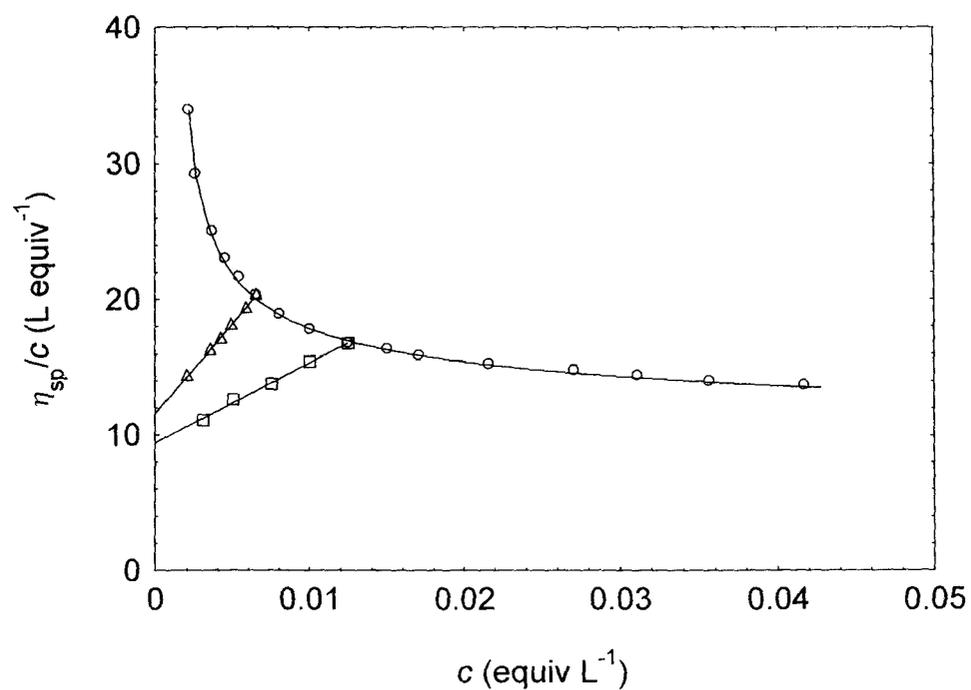
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<b><math>T = 308.15 \text{ K}</math></b>				
40	0.0065	$9.00 \pm 0.15$	$15.36 \pm 0.41$	0.9972
40	0.0125	$6.98 \pm 0.14$	$13.12 \pm 0.36$	0.9969
<b><math>T = 318.15 \text{ K}</math></b>				
40	0.0065	$9.75 \pm 0.20$	$11.09 \pm 0.45$	0.9934
40	0.0125	$7.56 \pm 0.18$	$10.13 \pm 0.40$	0.9939

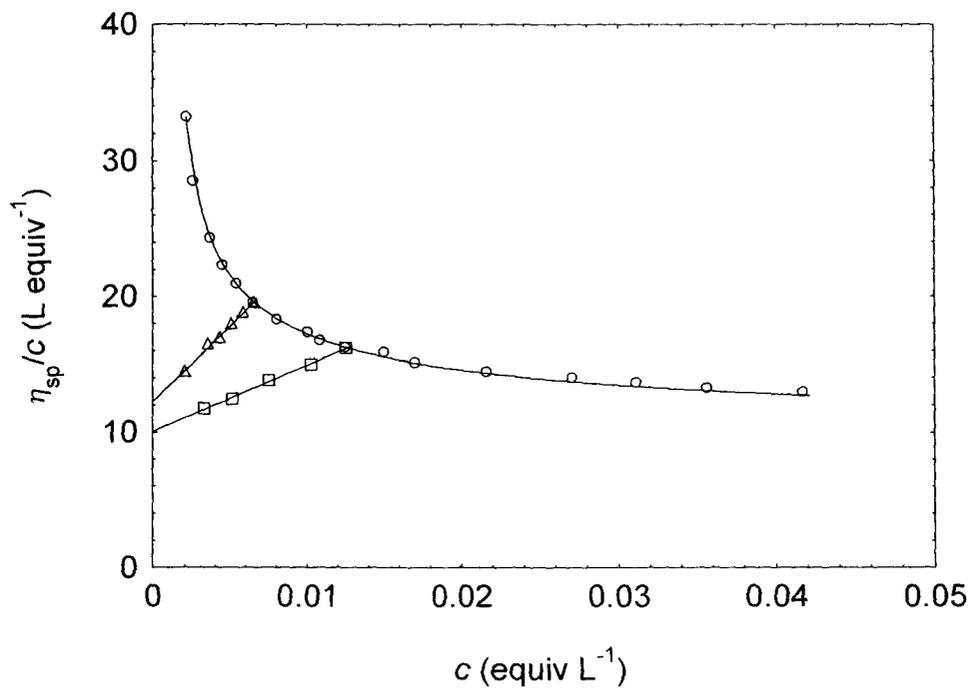
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**Table 2.** Parameters of Eq. (3) and the Correlation Coefficients of Fits (as  $r^2$ ) for Sodium Polystyrenesulfonate in Acetonitrile-Mater mixtures Containing 10, 20, and 40 vol percent of Acetonitrile

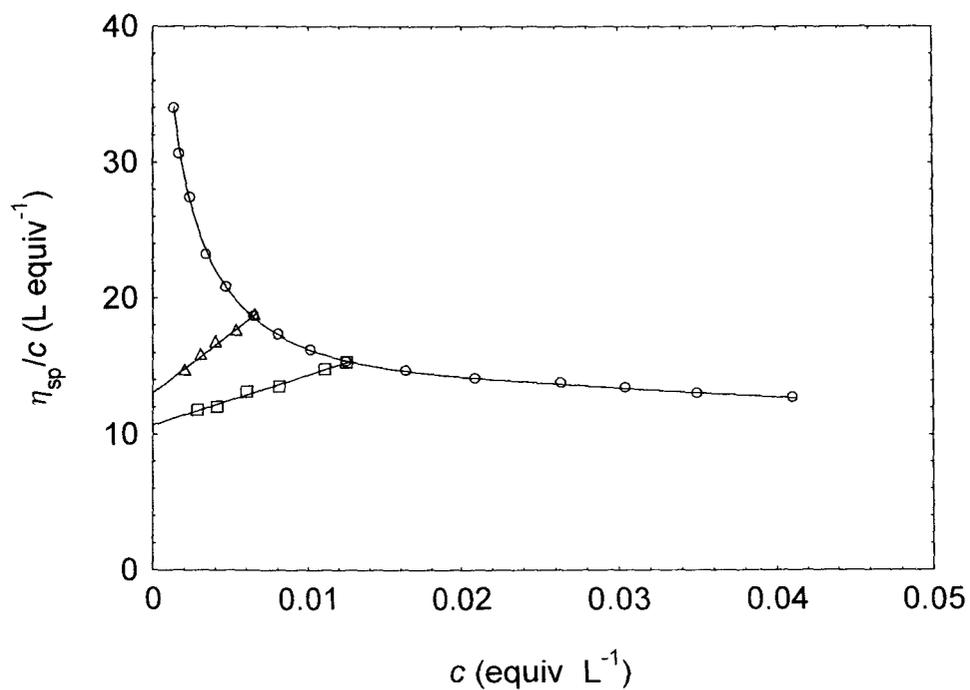
$c$ (equiv L <sup>-1</sup> )	$A$	$B$	$r^2$
<b>10 Vol Percent of Acetonitrile</b>			
0.0065	0.00048	-2966	0.992
0.0125	0.00013	-3235	0.994
<b>20 Vol Percent of Acetonitrile</b>			
0.0065	0.00097	-2864	0.997
0.0125	0.00109	-2733	0.999
<b>40 Vol Percent of Acetonitrile</b>			
0.0065	0.01410	-2138	0.951
0.0125	0.00749	-2297	0.998



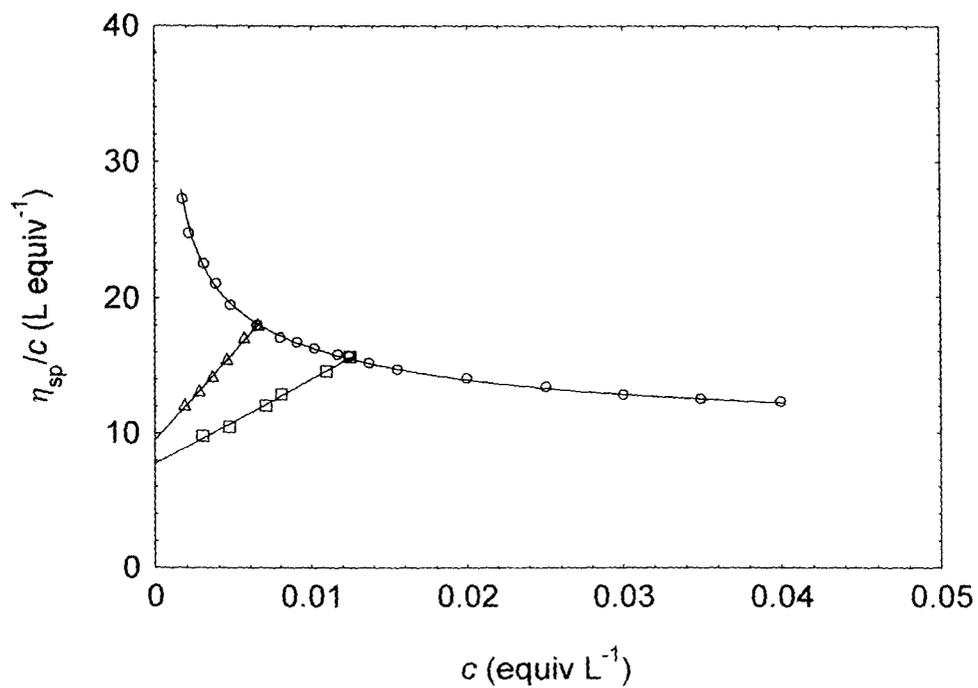
**Figure 1.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 298.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



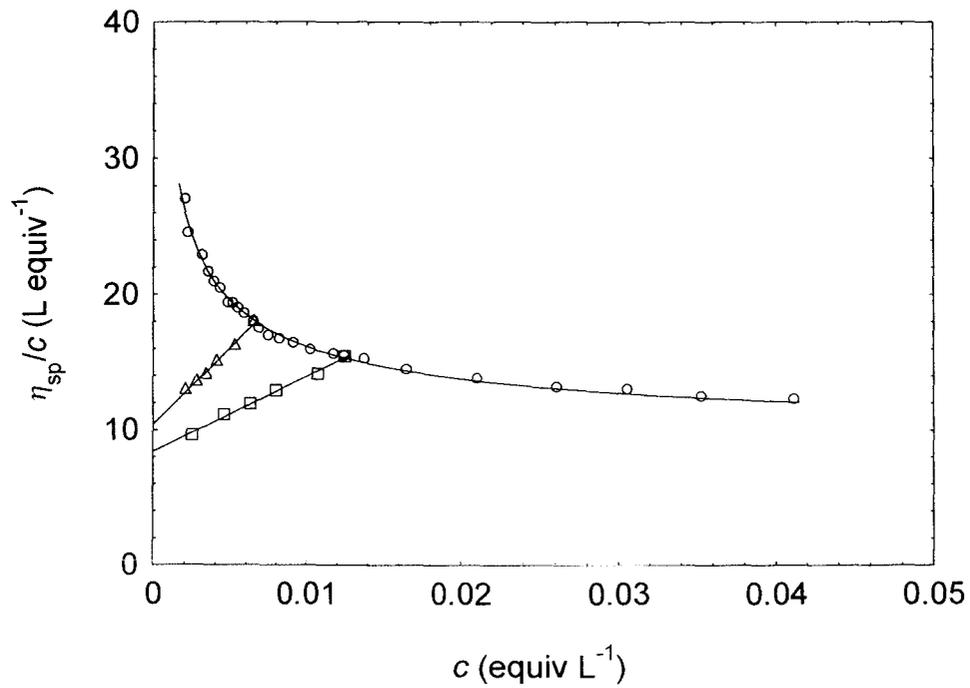
**Figure 2.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 308.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



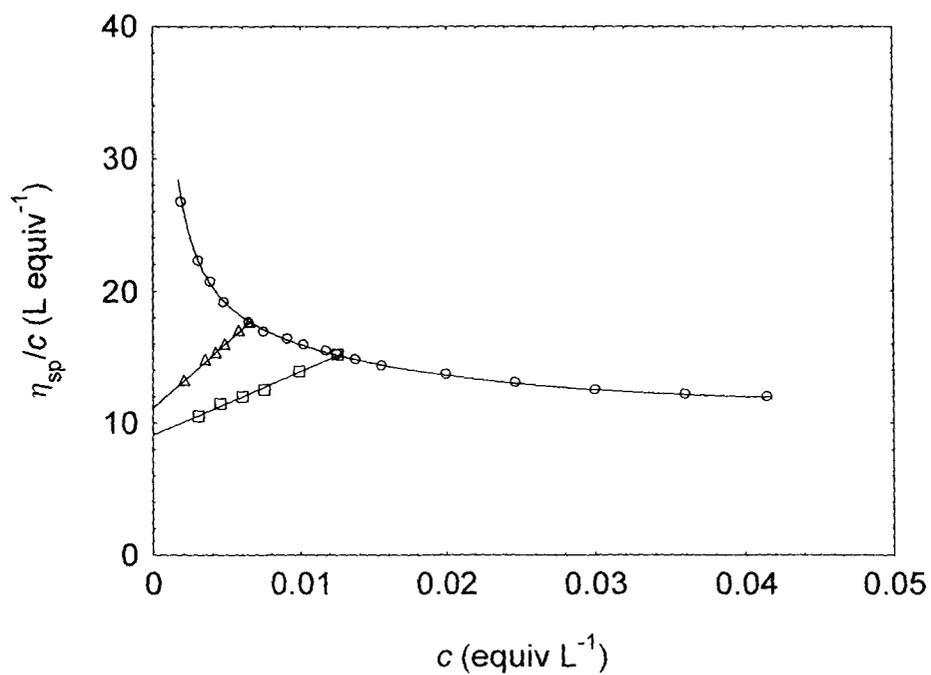
**Figure 3.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 318.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



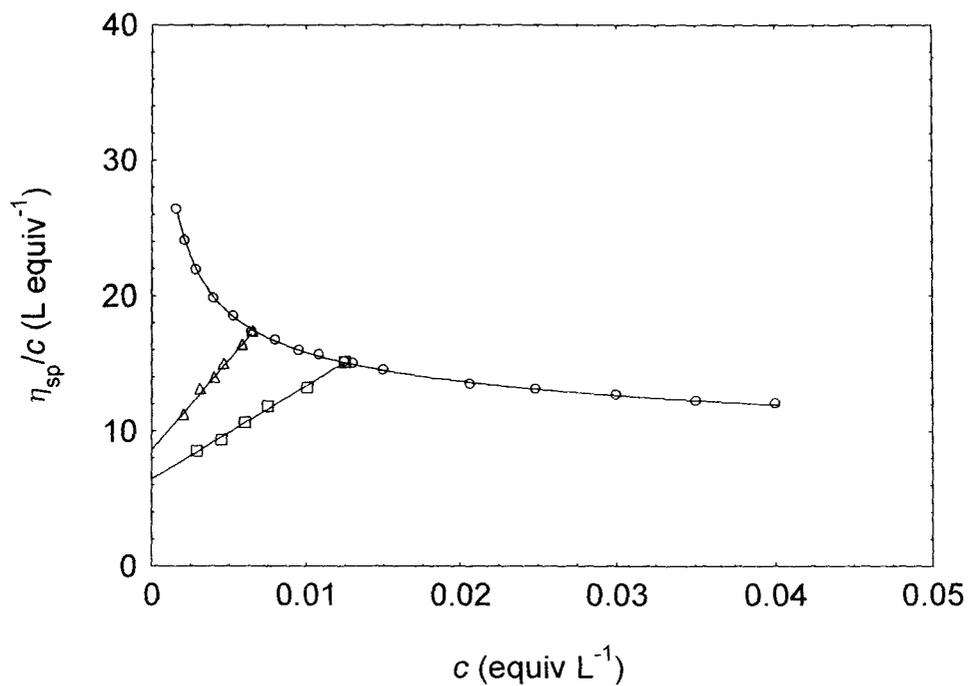
**Figure 4.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 298.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



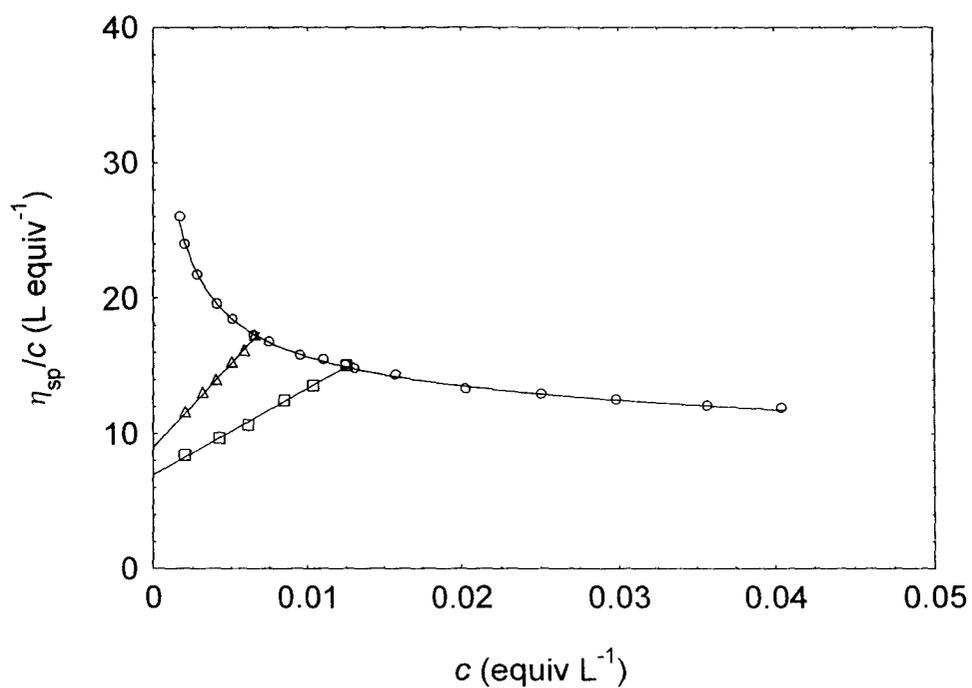
**Figure 5.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 308.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



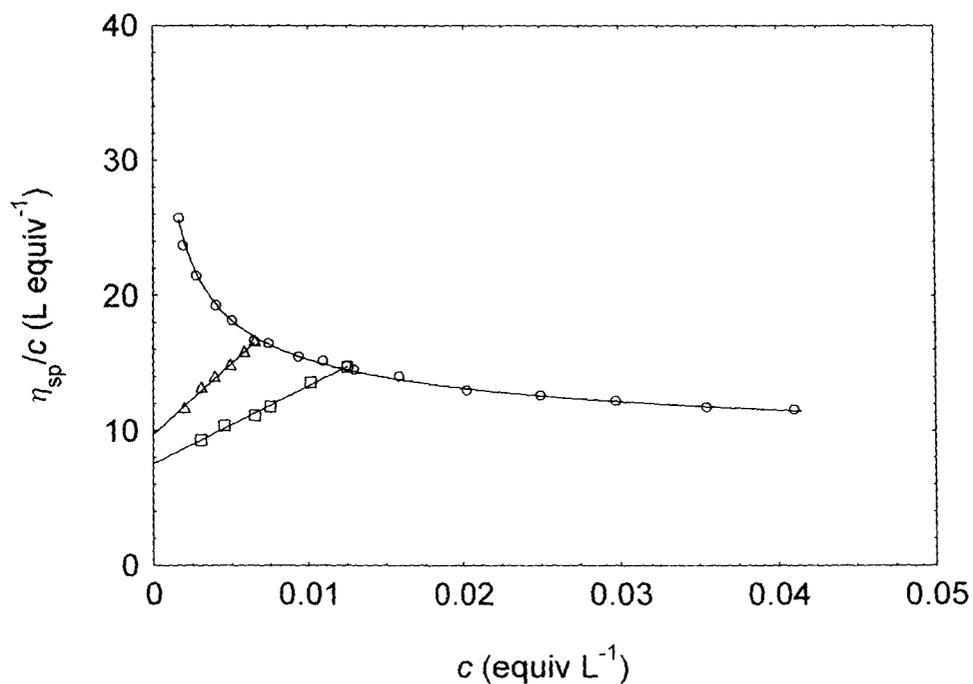
**Figure 6.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 318.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



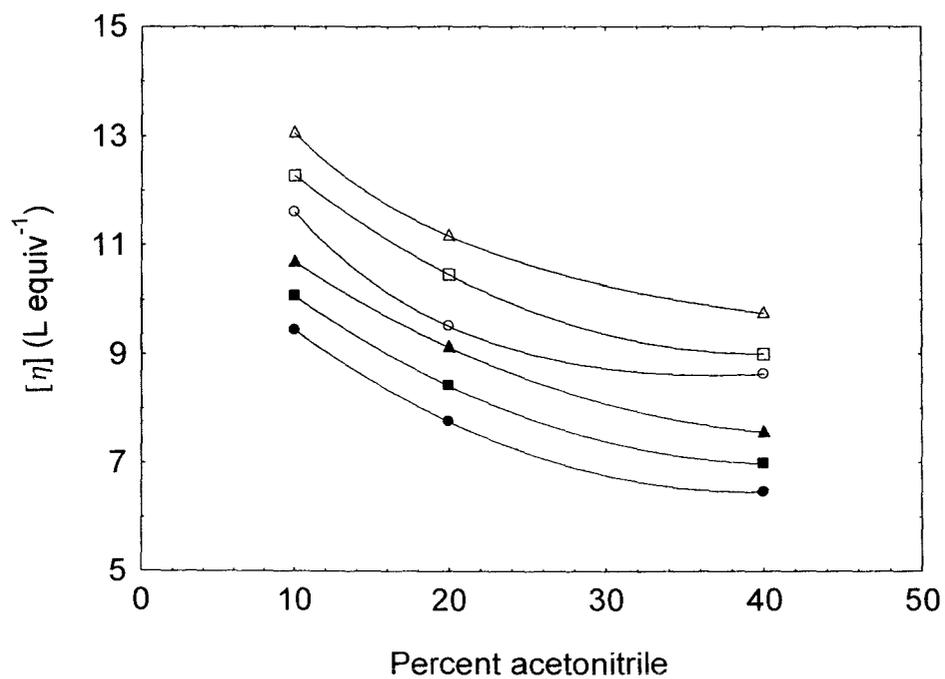
**Figure 7.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 298.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



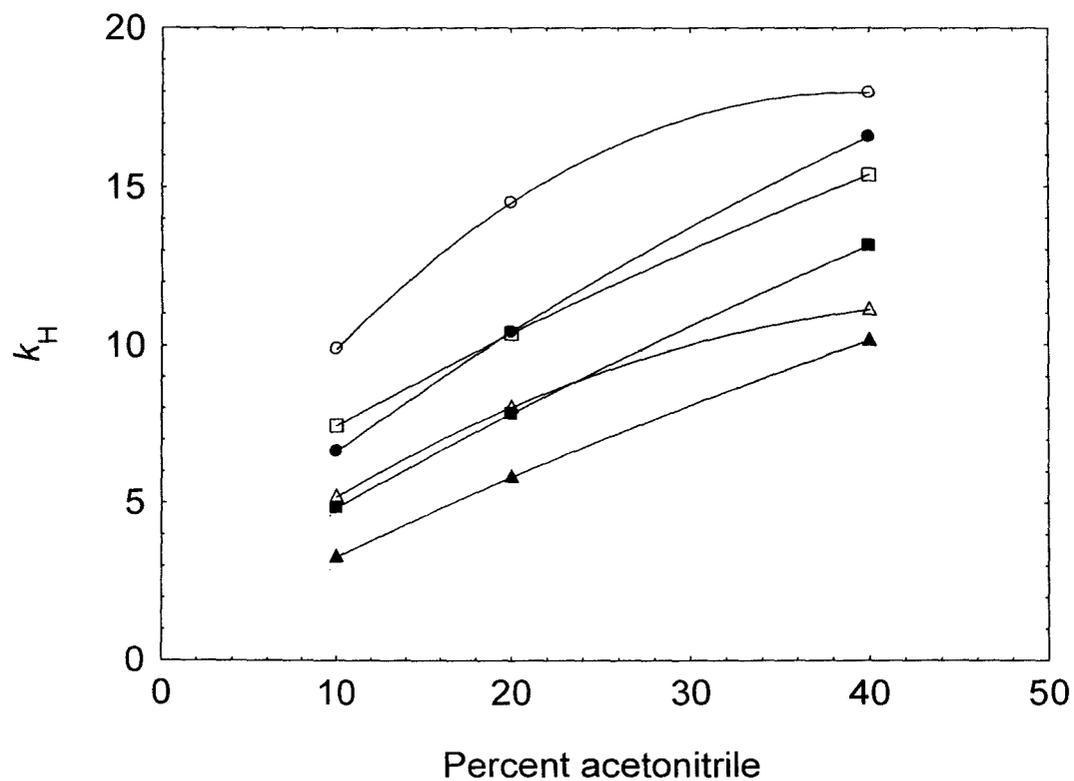
**Figure 8.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 308.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



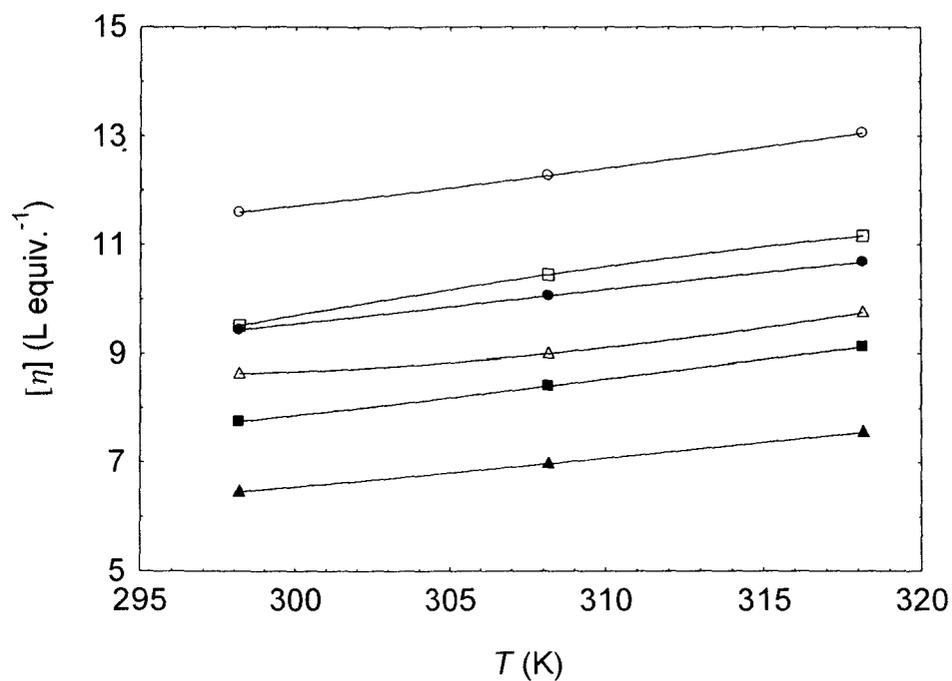
**Figure 9.** The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 318.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L<sup>-1</sup> (Δ), and 0.0125 equiv L<sup>-1</sup> (□) where isoionic dilutions were performed.



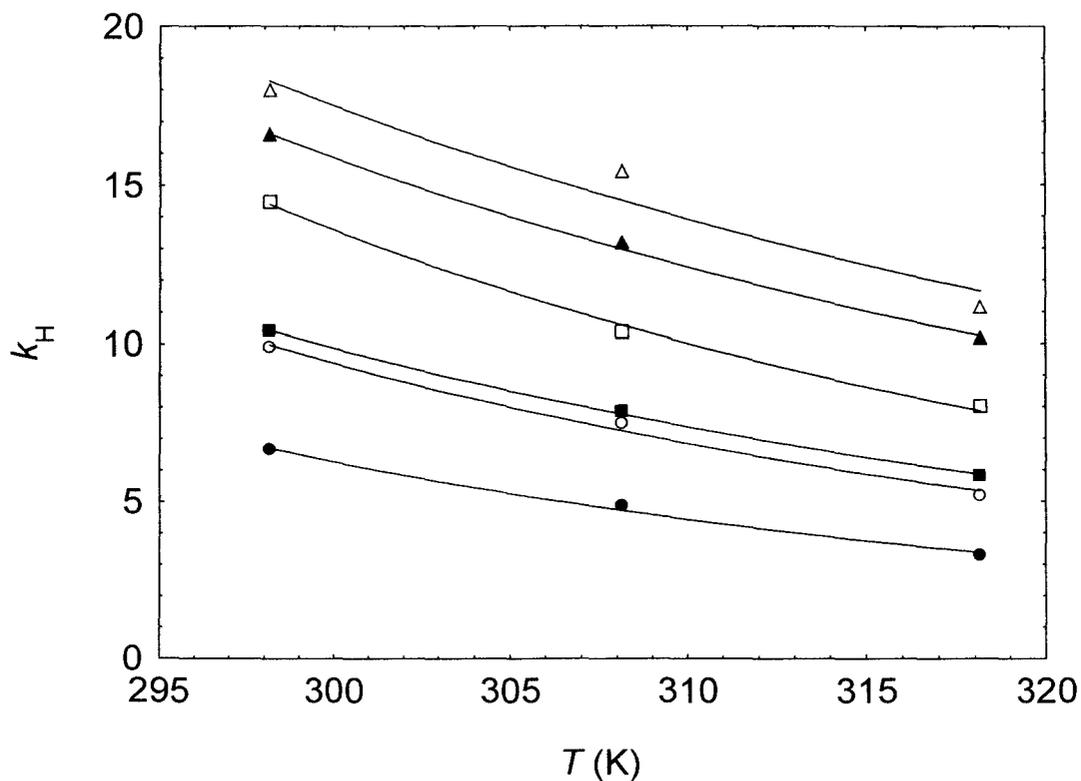
**Figure 10.** Effect of medium on the intrinsic viscosity for a polyelectrolyte concentration of  $0.0065 \text{ equiv L}^{-1}$  at  $298.15 \text{ K}$  ( $\circ$ ),  $308.15 \text{ K}$  ( $\square$ ), and  $318.15 \text{ K}$  ( $\Delta$ ); and for a polyelectrolyte concentration of  $0.0125 \text{ equiv L}^{-1}$  at  $298.15 \text{ K}$  ( $\bullet$ ),  $308.15 \text{ K}$  ( $\blacksquare$ ), and  $318.15 \text{ K}$  ( $\blacktriangle$ ).



**Figure 11.** Effect of medium on the Huggins constant for a polyelectrolyte concentration of  $0.0065 \text{ equiv L}^{-1}$  at  $298.15 \text{ K}$  ( $\circ$ ),  $308.15 \text{ K}$  ( $\square$ ), and  $318.15 \text{ K}$  ( $\Delta$ ); and for a polyelectrolyte concentration of  $0.0125 \text{ equiv L}^{-1}$  at  $298.15 \text{ K}$  ( $\bullet$ ),  $308.15 \text{ K}$  ( $\blacksquare$ ), and  $318.15 \text{ K}$  ( $\blacktriangle$ ).



**Figure 12.** Effect of temperature on the intrinsic viscosity for a polyelectrolyte concentration of 0.0065 equiv L<sup>-1</sup> in 10 vol percent acetonitrile-water mixture ( $\circ$ ), 20 vol percent acetonitrile-water mixture ( $\square$ ), and 40 vol percent acetonitrile-water mixture ( $\Delta$ ); and for a polyelectrolyte concentration of 0.0125 equiv L<sup>-1</sup> in 10 vol percent acetonitrile-water mixture ( $\bullet$ ), 20 vol percent acetonitrile-water mixture ( $\blacksquare$ ), and 40 vol percent acetonitrile-water mixture ( $\blacktriangle$ ).



**Figure 13.** Effect of temperature on the Huggins constant for a polyelectrolyte concentration of  $0.0065 \text{ equiv L}^{-1}$  in 10 vol percent acetonitrile-water mixture ( $\circ$ ), 20 vol percent acetonitrile-water mixture ( $\square$ ), and 40 vol percent acetonitrile-water mixture ( $\Delta$ ); and for a polyelectrolyte concentration of  $0.0125 \text{ equiv L}^{-1}$  in 10 vol percent acetonitrile-water mixture ( $\bullet$ ), 20 vol percent acetonitrile-water mixture ( $\blacksquare$ ), and 40 vol percent acetonitrile-water mixture ( $\blacktriangle$ ).

## Viscosity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media in Presence of NaCl

### Introduction

One of the most salient features of polyelectrolytes is the intense increment in viscosity that they produce when, even in minute amounts; they are dissolved in ordinary solvents in absence or in presence of a very small amount of an electrolyte, as described in the previous chapter. Early investigations of the anomalous viscosity of polyelectrolyte solutions without added appeared to suggest that the reduced viscosity would increase without limit as one lowers the polyelectrolyte concentration. In fact, the reduced viscosity versus concentration profile of a polyelectrolyte solution generally passes through a maximum whose position and height depend on the concentration of the added electrolyte. It is thus virtually impossible to obtain the intrinsic viscosity of a polyelectrolyte in salt-free solutions or in solutions containing a very small amount of an external salt by the method of extrapolation the Huggins equation<sup>1,2</sup>

$$\eta_{sp} / c = [\eta] + k_H [\eta]^2 c \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity describing the solvodynamic behaviour of the polymer molecules in solution,  $c$  is the polyelectrolyte concentration and  $k_H$  is the Huggins constant which is a characteristic for a given polymer-solvent system.

In the previous chapter, we have used the method of isoionic dilution for the determination of the intrinsic viscosities of NaPSS in acetonitrile-water mixtures. 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.

On the other hand, in presence excess of low-molar-mass 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 polymer solution, thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation.<sup>1,2</sup>

This chapter describes the viscometric behaviour of NaPSS in absence and also in presence of an electrolyte (NaCl) in acetonitrile-water mixed solvent media. Our point of view is to focus on the role of electrostatic interactions on the viscosity of NaPSS in acetonitrile-water mixed solvent media. The intrinsic viscosities of NaPSS in these mixtures have also been determined.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 g.cm<sup>-3</sup> and a coefficient of viscosity of 0.3126 mPa.s at 308.15 K; these values are in good agreement with the literature values.<sup>3</sup> Triply distilled water with a specific conductance less than 10<sup>-6</sup> S.cm<sup>-1</sup> at 308.15 K was used for the preparation of the mixed solvents.

NaPSS employed in these investigations was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was 70,000 with a degree of substitution (DS) of 1, and these values agree well with those obtained from physiochemical characterization in the present study.

The viscometric measurements were performed at 308.15, using a Schultz-Immergut-type viscometer<sup>4</sup> with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within  $\pm 0.005$  K of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.<sup>5,6</sup> Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

To avoid moisture pick up, all of the solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

## Results and Discussion

We have measured the variation of reduced viscosity of NaPSS with polymer concentration in pure water as well as in acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 308.15 K. In each of these cases the effect of varying added salt concentration ( $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $5 \times 10^{-2}$ , and  $5 \times 10^{-1}$  mol L<sup>-1</sup> NaCl) was also investigated.

### *Variation of Reduced Viscosity with Polyelectrolyte Concentration*

The typical dependence of the reduced viscosity with polyelectrolyte concentration for the investigated systems are shown in Figures 1-3. In absence of an added electrolyte, the reduced viscosity is found to increase as polymer concentration decreases bending up at low polyelectrolyte concentration. From Figures 1-3 no maximum was, however, detected in the  $\eta_{sp}/c$  vs.  $c$  profile within the concentration range studied here in salt-free solutions as well as in solutions containing  $1 \times 10^{-4}$  mol L<sup>-1</sup> NaCl. In polymer solutions containing  $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  mol L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behavior, in which  $\eta_{sp}/c$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c$  greatly, and the maximum is shifted towards higher polymer concentration. This is a characteristic behaviour of the viscosity of polyelectrolyte solutions. This large decrease in the reduced viscosity can be explained by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. The maximum results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum of the reduced viscosity vs. polyelectrolyte concentration profiles, the pair potential has its maximum; it decreases upon dilution because of an increase in the intermolecular distances and also decreases with increasing concentration due to the screening of electrostatic interactions. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentration and, therefore, was close to the limit of accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations beneath the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

### ***Influence of Large Amount of Added Salt: Determination of Intrinsic Viscosity***

Figures 1-3 show the variation of  $\eta_{sp}/c$  as a function of  $c$  for five different salt concentration in each solvent composition at given experimental temperature. When the added salt concentration is sufficiently high (0.05 to 0.50 mol L<sup>-1</sup>), the polyelectrolyte effect was suppressed and a linear variation similar to that of neutral polymer solutions is observed. This is due to the screening of electrostatic interactions within and among the polyion chains. We were thus able to determine the intrinsic viscosity of NaPSS in acetonitrile-water mixed solvent media using the Huggins equation, Eq. (1).

From the present experimental  $\eta_{sp}/c$  vs.  $c$  data, the intrinsic viscosities and the Huggins constants were determined by the method of least squares using Eq. (1) and the results are given in Table 1 along with their standard errors and the correlation coefficients of fits (as  $r^2$ ).

The intrinsic viscosities of NaPSS in acetonitrile-water mixtures in presence of 0.5 mol L<sup>-1</sup> NaCl are always found to be significantly lower than the corresponding values obtained by the method of isoionic dilution maintaining total ionic strength at a very low level e.g.,  $6.50 \times 10^{-3}$  and  $1.25 \times 10^{-2}$  mol L<sup>-1</sup> (cf. Chapter VII). This indicates significant coiling of the polyion chains due to the relief of intrachain electrostatic repulsion (and hence decreasing  $k_H$ ) in presence of an excess of an added electrolyte. Moreover, in each of the three solvent mixtures investigated, the intrinsic viscosity value obtained with a salt concentration of 0.50 mol L<sup>-1</sup> is always found to be lower than that obtained with a salt concentration of 0.05 mol L<sup>-1</sup> indicating a more compact polyion structure in presence of higher amount of salt.

### ***Influence of Medium on the Intrinsic Viscosity and the Huggins Constant***

It can be seen from Table 1 that the intrinsic viscosities of NaPSS decrease as the solvent medium becomes richer in acetonitrile whereas a reverse trend is observed with the Huggins constants. This observation demonstrates that the solvent interacts with the polymer gradually poorly (i.e., with less thermodynamic affinity) as the medium gets richer in acetonitrile and hence the polymer-polymer contacts are becoming more probable than the polymer-solvent contacts, and therefore the solvodynamic dimension of the chain will be gradually reduced. This explains both the lower intrinsic viscosity and the higher values of

the Huggins constants in a solvent richer in acetonitrile. This is consistent with the general view that high  $k_H$  values are the characteristics of the poor solvents.<sup>7</sup>

## Conclusions

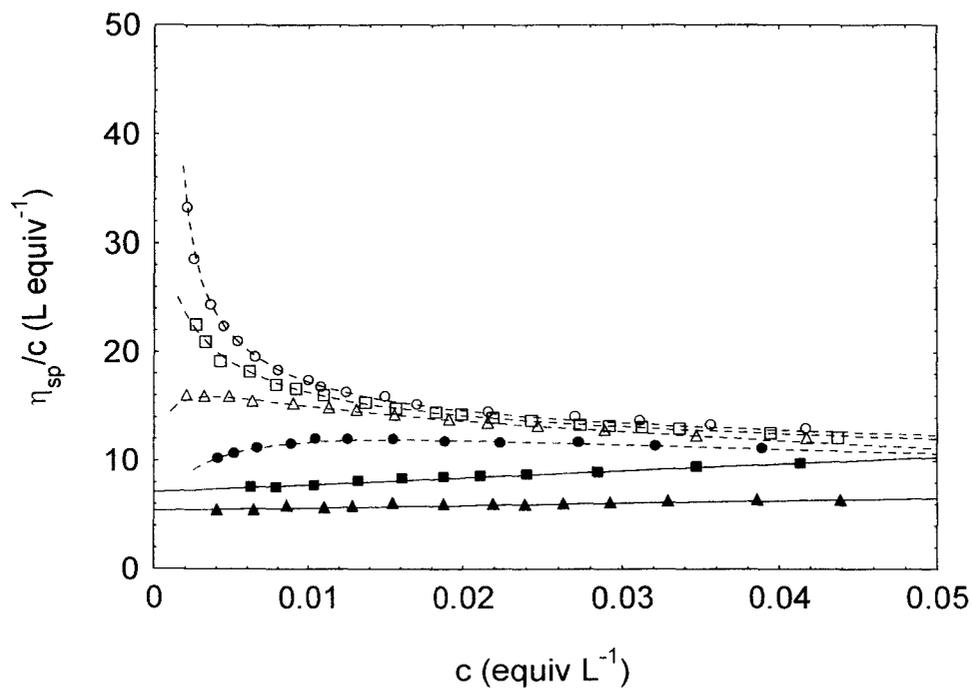
The present chapter reported precise measurements on the viscosities of the solutions of NaPSS in three acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 308.15 K in presence of varying concentration of added sodium chloride. The viscosity of the present system reveals the characteristic behaviour of polyelectrolyte solutions. In absence of added salt, the reduced viscosity is found to increase as polymer concentration decreases bending up at low concentration. No maximum was, however, detected in the  $\eta_{sp}/c$  vs.  $c$  profile within the concentration range studied here under salt-free conditions as well as in solutions containing  $1 \times 10^{-4}$  mol L<sup>-1</sup> NaCl. In polymer solutions containing  $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  mol L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behaviour, in which  $\eta_{sp}/c$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c$  greatly, and the maximum is shifted towards higher polymer concentration. This large decrease in the reduced viscosity can be explained by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. When the added salt concentration is sufficiently high (0.5 mol L<sup>-1</sup>), regular neutral polymer behaviour is recovered thus enabling us to determine the intrinsic viscosity of NaPSS in acetonitrile-water mixed solvent media using the Huggins equation. The variations of the intrinsic viscosity and the Huggins constant with temperature and solvent medium have been used to interpret the variation in the coiling of the polyion chain and counterion condensation.

## References

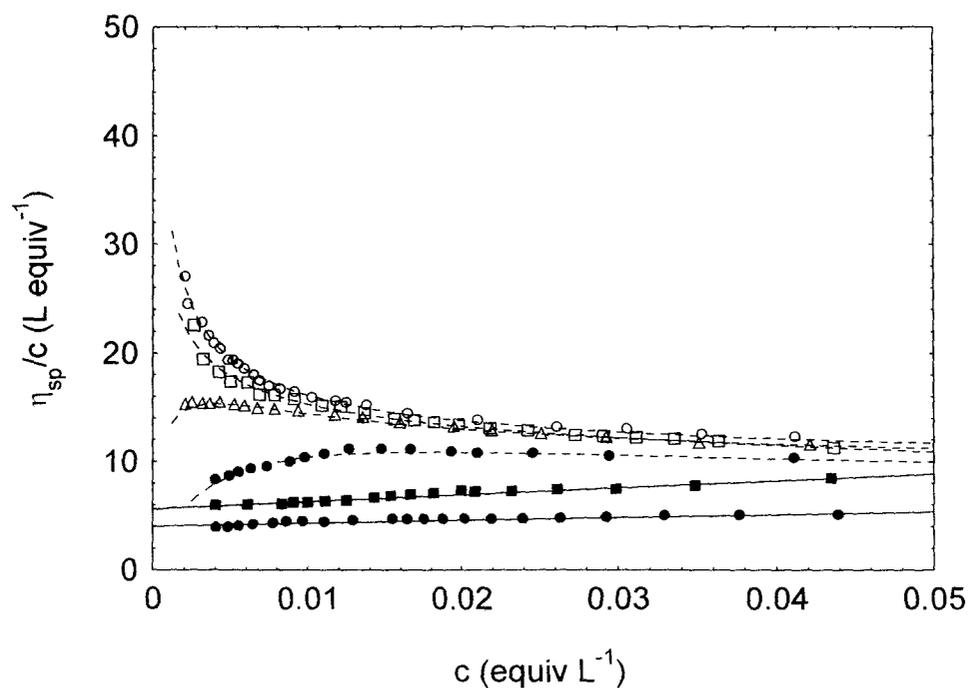
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**Table 1.** Intrinsic Viscosities  $[\eta]$  (L.equiv<sup>-1</sup>), Huggins Constants  $k_H$ , and the Correlation Coefficients of Fits (as  $r^2$ ) of NaPSS in 10, 20, and 40 Volume Percent Acetonitrile-Water Mixtures in Presence of 0.05 M and 0.50 mol L<sup>-1</sup> NaCl at 308.15 K

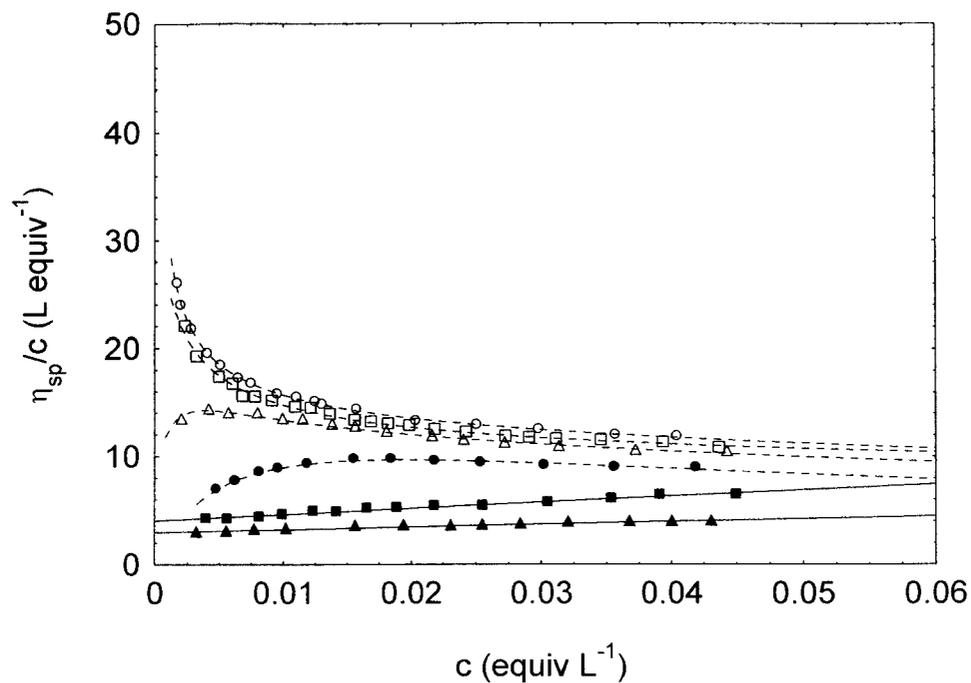
Conc of NaCl (mol L <sup>-1</sup> )		10 Vol Percent Acetonitrile	20 Vol Percent Acetonitrile	40 Vol Percent Acetonitrile
0.05	$[\eta]$ (L.equiv <sup>-1</sup> )	7.12 ± 0.07	5.64 ± 0.07	4.06 ± 0.07
	$k_H$	1.27 ± 0.06	2.03 ± 0.11	3.46 ± 0.17
	$r^2$	0.981	0.956	0.973
0.50	$[\eta]$ (L.equiv <sup>-1</sup> )	5.40 ± 0.07	4.06 ± 0.07	2.97 ± 0.05
	$k_H$	0.78 ± 0.10	1.57 ± 0.14	2.87 ± 0.21
	$r^2$	0.838	0.864	0.943



**Figure 1.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 10 volume percent acetonitrile at 308.15 K in presence of (○) 0 mol L<sup>-1</sup> NaCl, (□) 10<sup>-4</sup> mol L<sup>-1</sup> NaCl, (Δ) 10<sup>-3</sup> mol L<sup>-1</sup> NaCl, (●) 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, (■) 5 x 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, and (▲) 5 x 10<sup>-1</sup> mol L<sup>-1</sup> NaCl.



**Figure 2.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 20 volume percent acetonitrile at 308.15 K in presence of (○)  $0 \text{ mol L}^{-1}$  NaCl, (□)  $10^{-4} \text{ mol L}^{-1}$  NaCl, (Δ)  $10^{-3} \text{ mol L}^{-1}$  NaCl, (●)  $10^{-2} \text{ mol L}^{-1}$  NaCl, (■)  $5 \times 10^{-2} \text{ mol L}^{-1}$  NaCl, and (▲)  $5 \times 10^{-1} \text{ mol L}^{-1}$  NaCl.



**Figure 3.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 40 volume percent acetonitrile at 308.15 K in presence of (○)  $0 \text{ mol L}^{-1}$  NaCl, (□)  $10^{-4} \text{ mol L}^{-1}$  NaCl, (△)  $10^{-3} \text{ mol L}^{-1}$  NaCl, (●)  $10^{-2} \text{ mol L}^{-1}$  NaCl, (■)  $5 \times 10^{-2} \text{ mol L}^{-1}$  NaCl, and (▲)  $5 \times 10^{-1} \text{ mol L}^{-1}$  NaCl.

## Chapter VIII

### Apparent Molar Volumes of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media

#### Introduction

The principal 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 related to expansibility of the polymer chains, while the second is not only reflected in counterion binding but also in the extent of solvation and the structure of the solvent in the vicinity of polyelectrolytes. Both of these factors are associated with the relative permittivity of the solvent media. Use of a series of mixed solvents gives rise to a systematic variation in the relative permittivity of the media and hence allows investigation on these interactions prevailing in polyelectrolyte solutions. We have already investigated the influence of intramacromolecular electrostatic repulsions and the resulting coiling/expansion of the polyion chains from viscosity measurements on NaPSS in acetonitrile-water mixtures (*cf.* Chapters VI and VII). In this chapter, we report the apparent molar volumes of NaPSS in acetonitrile-water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

#### Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of  $0.76570 \text{ g.cm}^{-3}$  and a co-efficient of viscosity of  $0.3126 \text{ mPa.s}$  at  $308.15 \text{ K}$ ; these values are in good agreement with the literature values.<sup>1</sup> Triply distilled water with a specific conductance of less than  $10^{-6} \text{ S.cm}^{-1}$  at  $308.15 \text{ K}$  was used for the preparation of the mixed solvents.

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was  $70 \text{ kDa}$ .

The densities were measured with an Ostwald-Sprengel pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about  $1 \text{ mm}$ . The pycnometer was calibrated at the experimental temperatures with deionized distilled water, methanol and acetonitrile. Measurements were made in a water bath maintained within  $\pm 0.005 \text{ K}$  of the

experimental temperature. The precision of the density measurements was always within  $\pm 3 \times 10^{-5} \text{ g.cm}^{-3}$ . Densities of acetonitrile-water mixtures at 298.15, 308.15, and 318.15 K are given in Table 1.

## Results and Discussion

### *Apparent Molar Volumes*

The apparent molar volumes ( $\phi_v$ ) of the polyelectrolyte in solution can be calculated using the conventional equation

$$\phi_v = \frac{M}{\rho_0} - 1000 \frac{(\rho - \rho_0)}{c\rho_0} \quad (1)$$

where  $c$  is the polyelectrolyte concentration (in monomolarity),  $M$  the molecular mass of the repeating unit of NaPSS with a degree of substitution (DS) of 1,  $\rho$  the density of the solution and  $\rho_0$  the density of the solvent.

### *Variations of Apparent Molar Volumes with Polyelectrolyte Concentration*

Figures 1 – 3 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of NaPSS in acetonitrile-water mixtures in 10, 20 and 40 volume percent of acetonitrile in acetonitrile-water mixtures at 298.15, 308.15, and 318.15 K. Within the concentration ranges investigated here, the  $\phi_v$  vs.  $\sqrt{c}$  plots are found to be linear and, moreover, as  $\sqrt{c}$  is increased,  $\phi_v$  increased slightly. Similar linear increases for  $\phi_v$  with concentration have been previously reported by Conway and Desnoyers,<sup>2</sup> Lawrence and Conway,<sup>3</sup> Ise and Okubo<sup>4</sup> and Tondre and Zana<sup>5</sup> for various polyelectrolytes in aqueous solutions although the insensitivity of  $\phi_v$  toward concentration was also reported<sup>4</sup> for salts of polystyrenesulfonic acid and polyethylenimine in water. It should be pointed out that the concentration dependences observed in the present study are small compared to those for most simple electrolytes. The possible explanation for the positive slopes in acetonitrile-water mixed solvent media might be that counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. As a consequence, contraction of the solvent medium would be lowered with increasing concentration of the polyelectrolyte, resulting in a net positive volume change per monomole of the added polyelectrolyte, and, therefore, in a positive slope of the  $\phi_v$  vs.  $\sqrt{c}$

plots. Moreover, at a given temperature a slight increase in the values of the slopes with increasing amount of acetonitrile in acetonitrile-water mixture was also observed. This indicates a greater polyion-counterion interaction as the solvent medium becomes richer in acetonitrile. Exactly the same conclusion regarding the counterion-binding behaviour of NaPSS in the present mixed solvent media has been drawn from our conductometric studies (*cf.* Chapter IV).

### ***The Limiting Partial Molar Volumes***

The apparent molar volumes at infinite dilution,  $\phi_v^0$  (equal to the limiting partial molar volumes,  $V_2^{\bar{0}}$ ) were obtained by least-squares fitting of  $\phi_v$  values to the equation

$$\phi_v = \phi_v^0 + S_v \sqrt{c} \quad (2)$$

where  $S_v$  is the experimental slope. The values of  $\phi_v^0$  ( $= V_2^{\bar{0}}$ ) and  $S_v$  are given Table 2. The correlation coefficients ( $r$ ) of the regression analyses were always found to be greater than or equal to 0.968.

The limiting partial molar volumes are found to decrease as the medium becomes richer in acetonitrile at a given temperature, whereas in a given mixed solvent medium,  $V_2^{\bar{0}}$  values are found to increase with increasing temperature.

### ***Ionic Limiting Partial Molar Volumes***

In order to investigate the specific behaviour of the polyion and the counterion comprising the polyelectrolyte, it is necessary to split the  $V_2^{\bar{0}}$  values into their ionic components. Now, the limiting partial molar volumes of sodium ion could be obtained from the literature  $V_2^{\bar{0}}$  values of NaCl, sodium tetraphenylborate (NaBPh<sub>4</sub>), and tetraphenylphosphonium chloride (Ph<sub>4</sub>PCl) in acetonitrile-water mixtures at 298.15 K<sup>6</sup> by employing the tetraphenylphosphonium tetraphenylborate (TPTB) assumption.<sup>7</sup> We, therefore, have separated the limiting partial molar volumes of NaPSS in acetonitrile-water mixtures at that particular temperature. The limiting partial molar volumes of sodium ion are, however, not available at the relevant compositions of the acetonitrile-water mixtures at which our measurements have been carried out. The available values of the limiting partial molar volumes of NaCl, NaBPh<sub>4</sub>, and Ph<sub>4</sub>PCl in acetonitrile-water mixtures at 298.15 K were, therefore, plotted against the volume per cent of acetonitrile in acetonitrile-water

mixtures and the  $V_2^{\bar{0}}$  values of these electrolytes at the desired compositions have been generated from the smooth master curves. These were then employed to obtain the limiting partial molar volume of sodium ion *via* the TPTB assumption.

### ***Various Contributing Factors to the Ionic Limiting Partial Molar Volumes***

Following Millero,<sup>8,9</sup> the ionic limiting partial molar volume,  $V_{\text{ion}}^{\bar{0}}$ , can be attributed to the following components

$$V_{\text{ion}}^{\bar{0}} = V_{\text{intr}}^{\bar{0}} + V_{\text{elec}}^{\bar{0}} + V_{\text{str}}^{\bar{0}} + V_{\text{cage}}^{\bar{0}} \quad (3)$$

where  $V_{\text{intr}}^{\bar{0}}$  is the intrinsic partial molar volume (the positive increment in the  $V_{\text{ion}}^{\bar{0}}$  value due to intrinsic volume of the ion; as a rule an intrinsic ionic volume in a solution is considered to be equal to its crystallographic volume<sup>10</sup>),  $V_{\text{elec}}^{\bar{0}}$  is the electrostriction partial molar volume (the negative increment equal to the decrease in molar solute volume due to ion-solvent electrostrictive interaction),  $V_{\text{str}}^{\bar{0}}$  is the disordered or void-space partial molar volume (the increment due to the destruction of solvent structure in the region of the ionic co-sphere) and  $V_{\text{cage}}^{\bar{0}}$  is the caged partial molar volume (the negative increment characteristic of solvophobic “structure-making” parts of the ions in solution, due to the filling of the intermolecular cavities of the solvent structure).

It may be pointed out that the electric forces due to the negative charges on the structural units of NaPSS affect strongly the surrounding solvent molecules and hence for the carboxymethylcellulose polyion,  $V_{\text{elec}}^{\bar{0}}$  will contribute significantly to its limiting partial molar volume. Because of the polar nature of acetonitrile-water mixtures, the apolar part will also contribute to the polyion limiting partial molar volume through the term  $V_{\text{cage}}^{\bar{0}}$ . Sodium ion, on the other hand, has nothing to do with caged partial molar volume.

### ***Effect of Medium and Temperature on the Limiting Partial Molar Volumes***

Table 3 shows that the limiting partial molar volume of the polyion decreases with increasing amount of acetonitrile in the acetonitrile-water mixtures. This indicates that the total contribution of the terms  $V_{\text{elec}}^{\bar{0}}$  and  $V_{\text{cage}}^{\bar{0}}$  becomes more important over that of the term  $V_{\text{str}}^{\bar{0}}$  as the solvent medium becomes richer in acetonitrile. This is a manifestation of the

predominance of the combined influence of the polyion-solvent electrostrictive interaction and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium. For sodium ion, on the other hand, the disordered partial molar volume plays the leading role. In case of the polyelectrolyte as a whole, however, the polyion is governing the solution behaviour. Here also the limiting partial molar volume of NaPSS decreases with increasing amount of acetonitrile in the acetonitrile-water mixtures (Table 2) like the polyion. An increase in the temperature increases the limiting partial molar volume of NaPSS in a given mixed solvent medium as can be seen from Table 2. This might be ascribed to the growing importance of the disordered partial molar volume due to a temperature-induced desolvation of the counterion leading to more counterion binding at higher temperatures as observed earlier from conductivity measurements (Chapter IV).

## **Conclusions**

The present investigation indicates that in acetonitrile-water mixed solvent media counterion binding would become quite appreciable as the concentration of the sodium polystyrene sulfonate is increased, thereby weakening the ion-solvent interactions. Moreover, the polyion is found to govern the volumetric behaviour of the polyelectrolyte as a whole in these solutions. The predominance of the combined influence of the polyion-solvent electrostrictive interactions and the solvophobic filling of the intermolecular cavities of the solvent structure by the apolar parts of the polyion with increasing acetonitrile content in the medium was observed. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

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**Table 1.** Densities,  $\rho$  ( $\text{g cm}^{-3}$ ) of Acetonitrile-Water Mixed Solved Media at 298.15, 308.15, and 318.15 K

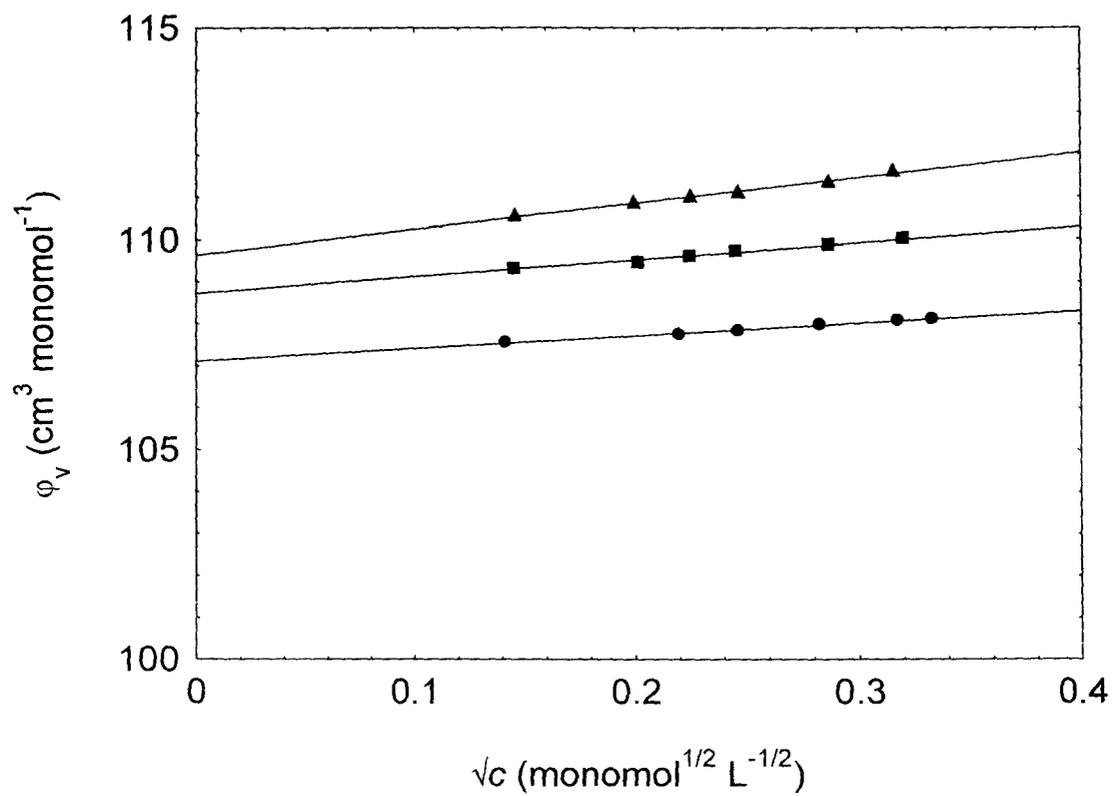
<i>T</i> (K)	$\rho$ ( $\text{g cm}^{-3}$ )		
	Vol Percent of Acetonitrile		
	10	20	40
298.15	0.98307	0.97046	0.93800
308.15	0.98096	0.96485	0.92362
318.15	0.97625	0.95912	0.91542

**Table 2.** Limiting Partial Molar Volumes,  $V_2^0$  ( $\text{cm}^3 \text{ monomol}^{-1}$ ) of NaPSS in Acetonitrile-Water Mixed Solved Media at 298.15, 308.15, and 318.15 K

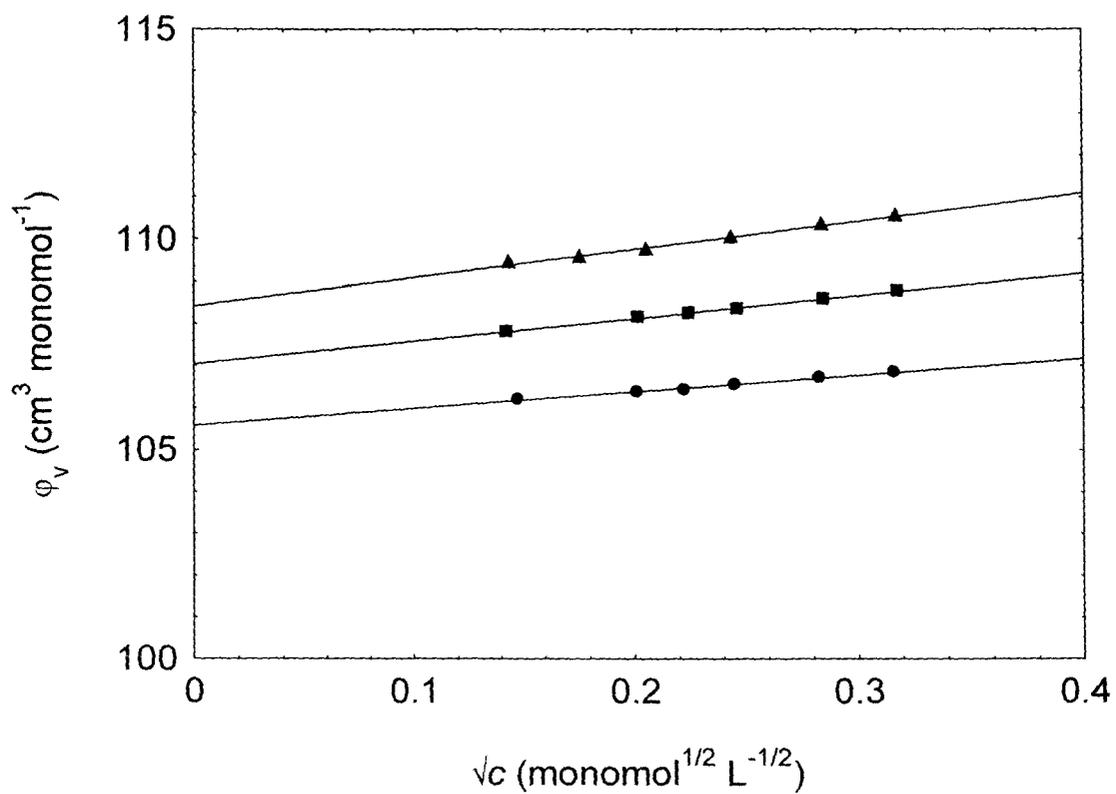
$T$ (K)	$V_2^0$ ( $\text{cm}^3 \text{ monomol}^{-1}$ )		
	Vol Percent of Acetonitrile		
	10	20	40
298.15	$107.10 \pm 0.04$	$105.58 \pm 0.04$	$102.73 \pm 0.05$
308.15	$108.72 \pm 0.09$	$107.04 \pm 0.03$	$105.07 \pm 0.05$
318.15	$109.64 \pm 0.07$	$108.41 \pm 0.07$	$106.41 \pm 0.04$

**Table 3.** Limiting Partial Molar Volumes,  $V_2^{\bar{0}}$  [(cm<sup>3</sup> mol<sup>-1</sup>) or (cm<sup>3</sup> monomol<sup>-1</sup>)] of Sodium Ion (Na<sup>+</sup>) and Polystyrenesulfonate Ion (PSS<sup>-</sup>) in Acetonitrile-Water Mixed Solved Media at 298.15 K

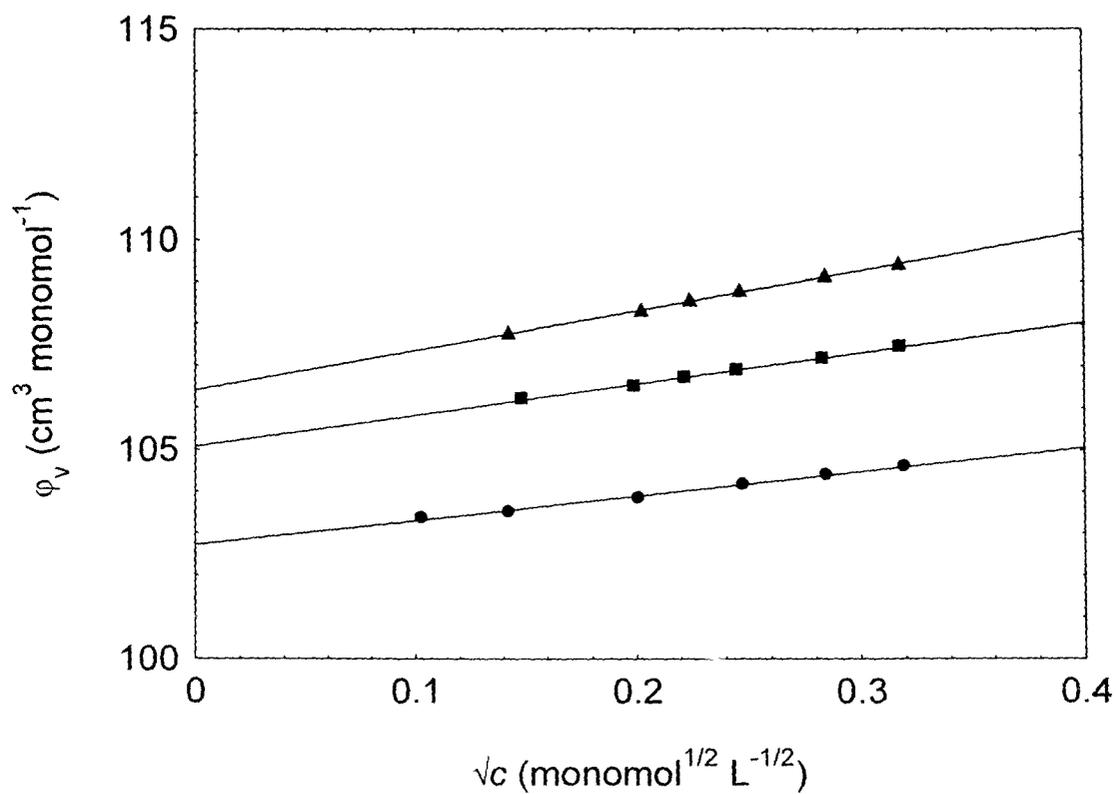
Ion/Polyion	$V_2^{\bar{0}}$ [(cm <sup>3</sup> mol <sup>-1</sup> ) or (cm <sup>3</sup> monomol <sup>-1</sup> )]		
	Vol Percent of Acetonitrile		
	10	20	40
Na <sup>+</sup>	-9.12	-7.14	-3.35
PSS <sup>-</sup>	116.22	112.72	106.08



**Figure 1.** Apparent molar volumes of NaPSS in 10 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K (●), 308.15 K (■), and 318.15 K (▲).



**Figure 2.** Apparent molar volumes of NaPSS in 20 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K ( $\bullet$ ), 308.15 K ( $\blacksquare$ ), and 318.15 K ( $\blacktriangle$ ).



**Figure 3.** Apparent molar volumes of NaPSS in 40 vol percent of acetonitrile in acetonitrile-water mixed solvent medium at 298.15 K (●), 308.15 K (■), and 318.15 K (▲).

## Chapter IX

# Sodium Polystyrenesulfonate-Induced Aggregation Behaviour of Cetyltrimethylammonium Bromide in Acetonitrile-Water Mixed-Solvent Media: A Conductivity and Tensiometric Study

### Introduction

Interactions between a polyelectrolyte and surfactant in aqueous solutions have been investigated for several decades and are extensively documented.<sup>1-5</sup> In particular, there have been significant research efforts focusing on the interactions between polyelectrolytes and oppositely charged surfactants in recent years.<sup>5-23</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>24,25</sup> While interactions between non-ionic polymers and ionic surfactants rely mainly on hydrophobicity,<sup>2,26</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>27</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>4,14,28-30</sup> enthalpies of binding,<sup>11,31</sup> and various thermodynamic and transport properties<sup>22,32</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>33,34</sup>

Although considerable attention has, so far, been paid to the investigations on the polymer-surfactant interactions in aqueous solutions,<sup>1-5</sup> such studies in mixed solvent media are scarce.<sup>21</sup> In mixed solvent systems, however, the dielectric constants of the media can be varied conveniently simply by changing the solvent composition. Hence the polyelectrolyte-surfactant interactions can be modified by changing the solvent composition due to the fact that the dominating electrostatic contributions to these interactions are largely influenced by the dielectric constant of the media. In particular, such study can give information about the influence of electrostatic effects on polyelectrolyte-surfactant interactions and on surfactant aggregation mediated by the polyelectrolyte as a function of the dielectric constant of the media.

Here, we investigate the aggregation behavior of cetyltrimethylammonium bromide (CTAB) in presence of varying concentration of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media containing 10, and 20 vol% of acetonitrile at temperatures 308.15, 313.15, and 318.15 K by using conductometry and tensiometry. Precipitation in the system above 20 vol% of acetonitrile prevented us to go beyond.

## Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of  $0.76570 \text{ g.cm}^{-3}$  and a co-efficient of viscosity of  $0.3126 \text{ mPa.s}$  at 308.15 K; these values are in good agreement with the literature values.<sup>35</sup> Triply distilled water with a specific conductance of less than  $10^{-6} \text{ S.cm}^{-1}$  at 308.15 K was used for the preparation of the acetonitrile-water mixed solvents.

The surfactant cetyltrimethylammonium bromide (CTAB) (E. Merck, Germany) has been used as received.

In the conductance method, a concentrated solution of CTAB, prepared in NaCl solution in the mixed solvents, was added in installments with the help of a microsyringe in the NaCl solution in the mixed solvents, placed in a wide mouth test tube fitted with a dip-type conductivity cell of cell constant  $1.15 \text{ cm}^{-1}$ . After each addition, conductance of the

solution was measured (after thorough mixing and temperature equilibration) with a Pye-Unicam PW9509 conductivity meter at a frequency of 2000 Hz. The cell was calibrated by the method of Lind *et al.*<sup>36</sup> using aqueous potassium chloride solutions. The measurements were triplicated. The conductance values were uncertain within the limit 0.01%.

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Several independent solutions were prepared and triplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within  $\pm 1 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$ .

Measurements were made at 308.15 K in a thermostated water-bath maintained within  $\pm 0.005 \text{ K}$ .

## Results and Discussion

### *Critical Micellar Concentrations (cmc) of Pure CTAB*

The critical micellar concentrations (*cmc*) of CTAB in absence of NaPSS were determined both from conductometry and tensiometry. These were obtained from the inflections in the plots of specific conductivity versus surfactant concentration. The data points above and below the inflection were fitted to two linear equations, and the *cmc*s were obtained from the intrersection. This method is found to be reliable and convenient for the present system because of the significant variations of specific conductivity with surfactant concentration in the pre- and postmicellar regions which allowed us to draw two unambiguous straight lines above and below the *cmc*. In tensiometry, the *cmc*s were the threshold surfactant concentrations required to saturate the air/solution interface and were obtained from the sharp breaks in the surface tension ( $\gamma$ ) versus log[surfactant] profiles. The representative plots for CTAB in 20 vol% acetonitrile at 313.15 K are shown in Figures 1 and 2a for tensiometry and conductometry, respectively. Similar plots were also observed for other systems. The *cmc* values of CTAB in two acetonitrile-water mixtures containing 10 and 20 vol% of acetonitrile at 308.15, 313.15, and 318.15 K are shown in Table 1. It is observed that in a given acetonitrile-water mixture the *cmc* of pure CTAB increases with increasing temperature within the range of temperature under study. Addition of acetonitrile shifts the *cmc* of CTAB to higher values at a given temperature (in water the *cmc*s of CTAB were

reported<sup>11</sup> to be 1.007 and 1.0900 mM from conductometry, and 1.102 and 1.200 mM from tensiometry respectively at 308.15, and 313.15 K). The *cmc* values are also found to increase as the medium gets richer in acetonitrile. Two factors must be considered to explain this significant influence of acetonitrile on the *cmc* value of CTAB: (a) the presence of acetonitrile decreases the cohesive energy density, or the solubility parameter, of water, thus increasing the solubility of the monomeric form of the surfactant and hence the *cmc*, and (b) the cosolvent causes a reduction in the relative permittivity of the aqueous phase, favouring the mutual repulsion of the ionic heads in the micelle, thus opposing micellisation and increasing the *cmc*.

### ***Critical Aggregation Concentrations (cac), Polymer Saturation Concentrations (psc), and Apparent Critical Micellar Concentrations (cmc\*) of NaPSS-CTAB***

The presence of NaPSS in CTAB solutions greatly modifies the tensiometric behavior of the surfactant. The  $\gamma$  -log[surfactant] curves of polyelectrolyte-surfactant systems display three distinct characteristic concentrations where the surface tension changes quite sharply. In presence of NaPSS, the first minimum in the plot is the critical aggregation concentration (*cac*) of CTAB. In this study, small aggregates started forming by the interaction of CTAB with the polyelectrolyte. Two processes, (1) binding of aggregates with NaPSS in the bulk and (2) binding of aggregates with NaPSS 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 NaPSS and CTAB 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\**). The *cmc\** is obviously higher than the corresponding *cmc* (*i.e.*, *cmc* of CTAB in absence of NaPSS). These characteristic features of  $\gamma$  versus log[surfactant] have been clearly demonstrated in the representative figure (Figure 1) for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol% acetonitrile at

313.15 K. These kinds of three-break tensiometric isotherms for interactions of polyvinylpyrrolidone with sodium dodecylsulfate were also reported earlier<sup>10</sup> for polyvinylpyrrolidone (PVP)-sodium dodecylsulfate (SDS) interactions. Park *et. al.*<sup>37</sup> also observed such complex tensiograms for aqueous solutions of CTAB in presence of NaPSS. These authors, however, did not report the characteristic CTAB concentrations for aggregate formation, polymer saturation and pure surfactant micelle formation in presence of NaPSS. Tensiometric profiles with lower complexity have also been reported sodium carboxymethylcellulose (NaCMC)-CTAB, and NaCMC-dodecyltrimethylammonium bromide (DTAB) systems<sup>14,38</sup> Chakraborty *et. al.*,<sup>11</sup> on the other hand, reported tensiograms with three breaks for NaCMC-CTAB interactions thus signifying the importance of both hydrophobic and electrostatic interactions. The values of *cac*, *psc*, and *cmc*\* from tensiometry are listed in Table 1.

We have also arrived at exactly the same conclusions concerning the NaPSS-CTAB interactions from conductometric (specific conductance versus surfactant concentration) profiles (*cf.* the representative Figure 2b for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol% acetonitrile at 313.15 K). The specific conductance versus surfactant concentration plots exhibit four linear regions (below the *cac*, between the *cac* and *psc*, between *psc* and *cmc*\*, and above the *cmc*\*, with gradually decreasing slopes where three distinct breaks are discernible. The three distinct breaks in the conductometric profiles were also observed for aqueous PVP-SDS system.<sup>10</sup> The values of *cac*, *psc*, and *cmc*\* obtained using conductometric procedure are included in Table 1; these are found to be in good agreement with the respective values derived from tensiometric measurements.

The *cmc*\* value obtained are always found to be higher than the *cmc* value in a given solvent medium and at a given temperatures for the two polyelectrolyte concentrations investigated. This indicates that the micelle formation in the presence of the polyelectrolyte is taking place at higher surfactant concentration due to the formation of polyelectrolyte-surfactant complex, which reduces the actual amount of surfactant molecules available for independent micellization.

### ***Variations of Critical Aggregation Concentration ( $cac$ ), Polymer Saturation Concentration ( $psc$ ), and Apparent Critical Micellar Concentration ( $cmc^*$ ) of NaPSS-CTAB with Polyelectrolyte Concentration, Temperature, and Solvent Composition of the Mixed Solvent Media***

From Table 1 it is apparent that the  $cac$  increases with the increase in NaPSS concentration in a given solvent medium at a given temperature. The increase in the  $cac$  value with the increase in the polyelectrolyte concentration is obviously related to the complexation of a greater amount of the surfactant. As the NaPSS concentration increases, more binding sites are available, and hence more surfactant ions bind to the polyion chain.

The  $cac$  values are also found to increase with the increase in temperature (Table 1). This means that replacement of the counterions of the polyelectrolyte by the surfactant ions increases with temperature. Another possible reason is the temperature-induced uncoiling of the polyion chain which results in more available binding sites at higher temperature for complex formation. A similar temperature dependence of the  $cac$  value for NaCMC-CTAB interaction was also noticed earlier by means of conductometry and microcalorimetry.<sup>11</sup>

Table 1 also indicates that at a given temperature and for a constant amount of polyelectrolyte, the  $cac$  values increase as the solvent medium becomes richer in acetonitrile *i.e.*, with the decrease in the relative permittivity of the solvent. This might be ascribed to the increase in the solubility of the hydrocarbon tail of the surfactant and polyelectrolyte chain with the increasing amount of acetonitrile in the mixed solvent media. As a result, the bound surfactants cluster side by side along the polyion chain and replace equal numbers of counterions from the polyelectrolyte molecule. An increase in the interaction between the polyion chain and surfactant ions with decreasing relative permittivity of the medium might also play an important role.

The variations of the  $psc$ , and  $cmc^*$  values for the present system also followed similar trends with polyelectrolyte concentration, solvent composition and temperature as those observed for the  $cac$  (mentioned earlier) thus corroborating the main conclusions drawn from the variation of  $cac$ .

### **Conclusions**

This chapter reports the aggregation behaviour of CTAB both in absence and in presence varying concentration of NaPSS in acetonitrile-water mixed solvent media at

308.15, 313.15, and 318.15 K. NaPSS induced self-aggregation of CTAB at a concentration much lower than its *cmc* values in the mixed solvent media. The system has evidenced different kinds of interacting features corresponding to polyelectrolyte-induced aggregate formation, CTAB aggregate-NaPSS binding in bulk, CTAB-NaPSS binding at the interface, and free micelle formation in solution. The critical aggregation concentrations (*cac*), polymer saturation concentrations (*psc*), and apparent critical micellar concentrations (*cmc*\*) for NaPSS-CTAB interactions have been determined from tensiometry and conductometry. Good agreement between the values obtained from these two techniques was found. The results have been discussed in terms of various interactions prevailing in the present system.

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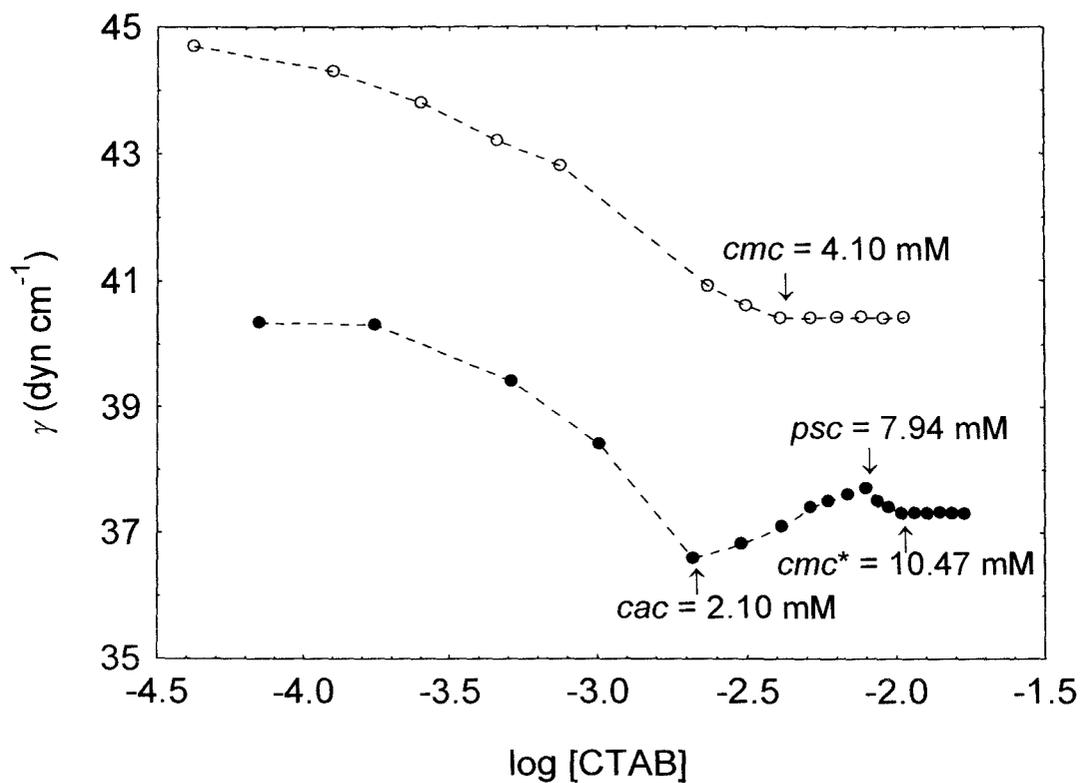
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**Table 1.** The Critical Aggregation Concentration (*cac*), Polymer Saturation Concentration (*psc*), Critical Micellar Concentration (*cmc*), and the Apparent Critical Micellar Concentration (*cmc\**) obtained from Tensiometry and Conductometry in Acetonitrile-Water Mixed Solvent Media Containing 10, and 20 Vol Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

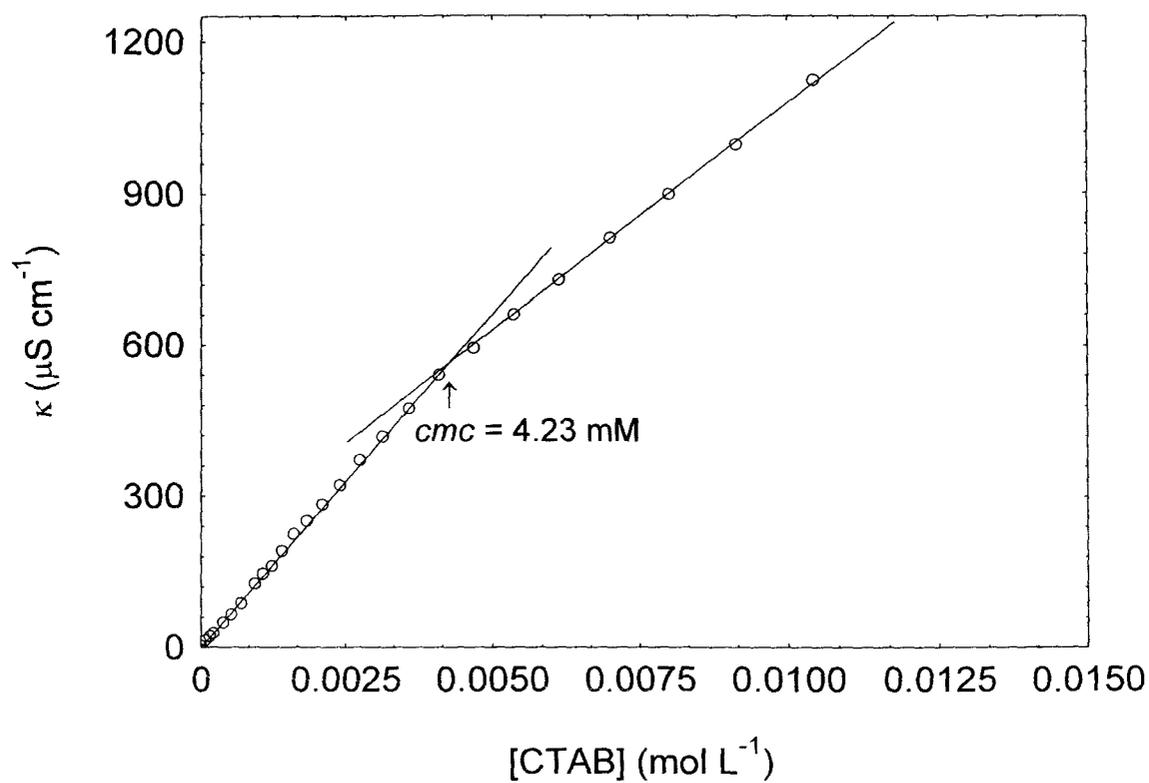
T (K)	[NaPSS] % (w/v)	<i>cac</i> (mM)	<i>psc</i> (mM)	<i>cmc</i> (mM)	<i>cmc*</i> (mM)	<i>cac</i> (mM)	<i>psc</i> (mM)	<i>cmc</i> (mM)	<i>cmc*</i> (mM)
		10 Vol Percent Acetonitrile				20 Vol Percent Acetonitrile			
308.15	0.00			3.03 <sup>a</sup>				3.54 <sup>a</sup>	
				3.24 <sup>b</sup>				3.87 <sup>b</sup>	
	0.01	1.45 <sup>a</sup>	3.97 <sup>a</sup>		6.80 <sup>a</sup>	1.54 <sup>a</sup>	5.95 <sup>a</sup>		9.44 <sup>a</sup>
		1.43 <sup>b</sup>	3.75 <sup>b</sup>		7.30 <sup>b</sup>	1.57 <sup>b</sup>	6.17 <sup>b</sup>		10.05 <sup>b</sup>
	0.02	1.71 <sup>a</sup>	4.44 <sup>a</sup>		9.12 <sup>a</sup>	1.86 <sup>a</sup>	6.76 <sup>a</sup>		10.47 <sup>a</sup>
		1.65 <sup>b</sup>	4.53 <sup>b</sup>		8.64 <sup>b</sup>	1.84 <sup>b</sup>	7.27 <sup>b</sup>		10.01 <sup>b</sup>
313.15	0.00			3.62 <sup>a</sup>				4.10 <sup>a</sup>	
				3.44 <sup>b</sup>				4.23 <sup>b</sup>	
	0.01	1.45 <sup>a</sup>	4.43 <sup>a</sup>		7.55 <sup>a</sup>	1.61 <sup>a</sup>	6.60 <sup>a</sup>		9.97 <sup>a</sup>
		1.49 <sup>b</sup>	4.10 <sup>b</sup>		7.60 <sup>b</sup>	1.74 <sup>b</sup>	7.04 <sup>b</sup>		10.22 <sup>b</sup>
	0.02	1.96 <sup>a</sup>	4.84 <sup>a</sup>		9.73 <sup>a</sup>	2.10 <sup>a</sup>	7.94 <sup>a</sup>		10.53 <sup>a</sup>
		1.91 <sup>b</sup>	5.07 <sup>b</sup>		9.50 <sup>b</sup>	2.20 <sup>b</sup>	7.64 <sup>b</sup>		10.98 <sup>b</sup>
318.15	0.00			4.56 <sup>a</sup>				5.24 <sup>a</sup>	
				4.25 <sup>b</sup>				5.13 <sup>b</sup>	
	0.01	1.47 <sup>a</sup>	4.98 <sup>a</sup>		8.34 <sup>a</sup>	1.78 <sup>a</sup>	7.28 <sup>a</sup>		10.23 <sup>a</sup>
		1.50 <sup>b</sup>	4.70 <sup>b</sup>		8.51 <sup>b</sup>	1.81 <sup>b</sup>	7.60 <sup>b</sup>		10.94 <sup>b</sup>
	0.02	1.98 <sup>a</sup>	5.35 <sup>a</sup>		10.45 <sup>a</sup>	2.23 <sup>a</sup>	8.06 <sup>a</sup>		11.63 <sup>a</sup>
		2.01 <sup>b</sup>	5.18 <sup>b</sup>		9.91 <sup>b</sup>	2.25 <sup>b</sup>	7.84 <sup>b</sup>		11.28 <sup>b</sup>

<sup>a</sup>Values obtained from tensiometry.

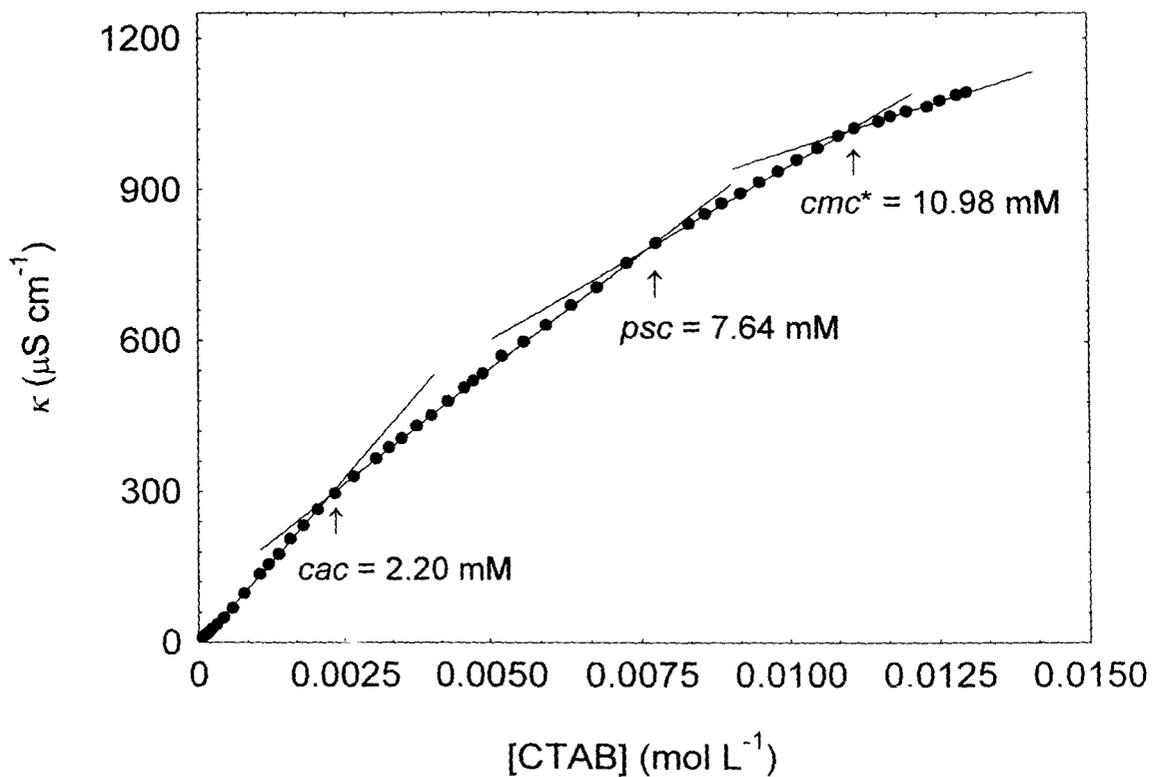
<sup>b</sup>Values obtained from conductometry.



**Figure 1.** Variation of  $\gamma$  with  $\log [\text{CTAB}]$  for CTAB and for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K, NaPSS concentration being 0.02% (w/v).



**Figure 2a.** Variation of the specific conductivity ( $\kappa$ ) with the concentration of CTAB in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K.



**Figure 2b.** Variation of the specific conductivity ( $\kappa$ ) with the concentration of CTAB in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K, NaPSS concentration being 0.02% (w/v).

## Chapter X

### Concluding Remarks

Polyelectrolytes show numerous interesting properties that are now being actively investigated in many laboratories. Many important information and concepts on aqueous polyelectrolyte solutions both in absence and in presence of low molar-mass electrolytes have been derived from studies on their electrical conductivity, viscosity and density. Moreover, studies on polyelectrolytes in presence of surfactants provide important information on polyelectrolyte-surfactant interactions. However, very little attention has been paid to polyelectrolyte solutions in absence as well as in presence of electrolytes and surfactants in mixed solvent media despite that fact that the study of polyelectrolytes in these media is important in the sense that such studies can offer insights into the understanding of fundamentals of polyelectrolytes; the effect of electrostatic interactions on the solution behaviour of polyelectrolytes can be investigated conveniently by varying the composition of the mixed solvent media and this is important in understanding the characteristic behaviour of polyelectrolytes. We have, therefore, investigated some transport and thermodynamic properties of sodium polystyrenesulfonate in acetonitrile-water mixed solvent media using the techniques mentioned above with special reference to polyelectrolyte-salt and polyelectrolyte-surfactant interactions with a view to obtain a precise information on the behavior of polyelectrolytes in such solutions.

Electrical conductivities provided valuable information on the condensation of counterions onto the polyion chain in salt-free solutions. A model put forward by Colby *et. al.* [*J. Polym. Sci. Part B: Polym. Phys.*, **35**, 2951 (1997)] using the scaling description proposed by Dobrynin *et. al.* [*Macromolecules*, **28**, 1859 (1995)] for the configuration of a polyelectrolyte chain in semidilute solution offered a sharp improvement over the Manning counterion condensation model. Electrical conductivities of the polyelectrolyte in presence of salts underlined the importance of various factors namely, electrophoretic countercurrent, solvodynamic interactions, salt-induced conformational changes in the polyion structure and hence a concomitant change in the apparent charge of the polyion *etc.* in polyelectrolyte solutions. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium in acetonitrile-water mixed solvent media. These were also obtained in presence of an excess of an added electrolyte where neutral polymer behaviour could be recovered. Viscosity studies shed light on the

coiling/expansion of the polyion chains in solvents with varying relative permittivities. The roles of electrostriction, solvophobicity and counterions condensation and their desolvation have been conveniently assessed from the partial molar volume studies. Studies on the influence of the solvent medium on the complexation of the present polyelectrolyte with a cationic surfactant, cetyltrimethylammonium bromide, and the aggregation of the surfactant molecules induced by the polyelectrolyte using conductometry and tensiometry provided important information on the polyelectrolyte-surfactant complexation and polyelectrolyte-induced aggregation behaviour.

However, it is necessary to remember that interactions in solutions containing polyelectrolytes are very complex in nature because of the coupling of the macromolecular properties with the electrolyte properties of these species. Investigation in mixed solvent media provide the opportunity to study the behaviour of polyelectrolyte solutions from a more general point of view compared to those in aqueous solutions since use of a series of mixed solvents corresponds to a gradual change in the relative permittivity of the media and hence in the interactions prevailing in these solutions. More extensive studies on the different thermodynamic and transport properties of a variety of polyelectrolytes both in absence and in presence of salts and surfactants in different mixed solvent media will be of immense help in understanding the nature of various interactions in polyelectrolyte solutions. A multi-method attack to this intricate problem - like the one presented here - might be very helpful in this regard.

## Appendix

# Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetrphenylborate, and Sodium Bromide in Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15 K: Determination of Limiting Ionic Equivalent Conductivities

## Introduction

In order to analyse the conductivity data of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media, the limiting equivalent conductivities of sodium ion in relevant mixture are essential. We have, therefore, performed electrical conductivity measurement on tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ), sodium tetrphenylborate ( $\text{NaBPh}_4$ ) and sodium bromide ( $\text{NaBr}$ ) in acetonitrile-water mixtures at 308.15, 313.15, and 318.15 K in order to obtain precise temperature-dependent single-ion conductivities since such data are practically nonexistent in mixed solvent media.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of  $0.76570 \text{ g}\cdot\text{cm}^{-3}$  and a coefficient of viscosity of  $0.3126 \text{ mPa}\cdot\text{s}$  at 308.15 K; these values are in good agreement with the literature values.<sup>1</sup> Triply distilled water with a specific conductance of less than  $10^{-6} \text{ S}\cdot\text{cm}^{-1}$  at 308.15 K was used for the preparation of the mixed solvents. The physical properties of acetonitrile-water mixed solvents used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1. The relative permittivities of acetonitrile-water mixtures at the experimental temperatures were obtained with the equations as described in the literature<sup>2</sup> using the literature density and relative permittivity data of the pure solvents<sup>1,3</sup> and the densities of the mixed solvents given in Table 1 of Chapter III .

All of these salts were of Fluka purum or puriss grade. Tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) was purified by recrystallization from acetone and the recrystallized salt was dried in vacuo at 333.15 K for 48 h. Sodium tetrphenylborate ( $\text{NaBPh}_4$ ) was recrystallized three times from acetone and then dried under vacuum at 353.15 K for 72 h. Sodium bromide ( $\text{NaBr}$ ) was dried in vacuo for 72 h immediately prior to use and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant  $1.15 \text{ cm}^{-1}$  and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers<sup>4</sup> using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within  $\pm 0.005 \text{ K}$  of the desired temperature. The details of the experimental procedure have been described earlier<sup>5,6</sup> and also in Chapter II. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about  $25 \text{ cm}^3$  capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the salt solutions.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in five replicates for each solution and at each temperature, and the results were averaged.

## Results and Discussion

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.<sup>7,8</sup> For a given set of conductivity values ( $\kappa_j$ ,  $\Lambda_j$ ;  $j = 1, \dots, n$ ), three adjustable parameters - the limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), and the association diameter ( $R$ ), are derived from the following set of equations :

$$\Lambda = p[\Lambda^0(1 + RX + EL)] \quad (1)$$

$$p = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \frac{\beta k}{2(1 + kR)} \quad (4)$$

$$\beta = \frac{e^2}{\epsilon k_B T} \quad (5)$$

$$K_A = K_R (1 + K_S) \quad (6)$$

where  $R_X$  is the relaxation field effect,  $EL$  is the electrophoretic countercurrent,  $\gamma$  is the fraction of unpaired ions, and  $\alpha$  is the fraction of contact-pairs,  $K_A$  is the overall pairing constant evaluated from the association constants of contact-pairs,  $K_S$ , of solvent-separated pairs,  $K_R$ ,  $\epsilon$  is the relative permittivity of the solvent,  $e$  is the electronic charge,  $k_B$  is the Boltzmann constant,  $k^{-1}$  is the radius of the ion atmosphere,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale, and  $\beta$  is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial  $A^0$  values for the iteration procedure were obtained from Shedlovsky extrapolation<sup>9</sup> of the data. Input for the program is the set  $(c_j, A_j; j = 1, \dots, n)$ ,  $n$ ,  $\epsilon$ ,  $\eta$ ,  $T$ , initial value of  $A^0$ , and an instruction to cover a preselected range of  $R$  values.

In practice, calculations are made by finding the values of  $A^0$  and  $\alpha$  which minimize the standard deviation,  $\sigma$ ,

$$\sigma^2 = \sum [A_j(\text{calcd}) - A_j(\text{obsd})]^2 / (n - 2) \quad (7)$$

for a sequence of  $R$  values and then plotting  $\sigma$  against  $R$ ; the best-fit  $R$  corresponds to the minimum in  $\sigma$  vs.  $R$  curve.

The values of  $A^0$ ,  $K_A$ , and  $R$  obtained by this procedure are reported in Table 1.

In order to investigate the specific behavior of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components.

The limiting ionic conductivities have been evaluated from the division of the  $A^0$  values of  $\text{Bu}_4\text{NBPh}_4$  using the following relationship:

$$\lambda^0(\text{Bu}_4\text{N}^+) = 0.517 A^0(\text{Bu}_4\text{NPh}_4\text{B}) \quad (8)$$

as described in the literature.<sup>10,11</sup>

The limiting molar conductivity ( $A^0$ ) of the "reference electrolyte"  $\text{Bu}_4\text{NBPh}_4$  was obtained by considering the Kohlrausch rule that allows the calculation of the  $A^0$  value for a

given electrolyte by the appropriate combination of others. The  $\Lambda^0$  values of  $\text{Bu}_4\text{NBr}$ ,  $\text{NaBPh}_4$  and  $\text{NaBr}$  obtained in the present solvent media have been used to obtain the  $\Lambda^0$  value of  $\text{Bu}_4\text{NBPh}_4$  through the following equation:

$$\Lambda^0(\text{Bu}_4\text{NBPh}_4) = \Lambda^0(\text{Bu}_4\text{NBr}) + \Lambda^0(\text{NaPh}_4\text{B}) - \Lambda^0(\text{NaBr}) \quad (9)$$

The limiting ionic conductances calculated from the above equations are recorded in Table 2.

The association constants ( $K_A$ ) listed in Table 1 for all these systems are practically negligible (*i.e.*,  $K_A < 10$ ). So, the numerical values of  $K_A$  should not be taken seriously.<sup>12</sup> One can only conclude that all of these three electrolytes exist as free ions in both the solvent mixtures in the temperature range 308.15 to 318.15 K. This is expected because the relative permittivities of the solvent mixtures are fairly high ( $57.32 \leq \epsilon \leq 67.94$ ).

The cosphere diameter ( $R$ ) values for all the salts under study in the acetonitrile-water mixtures are also reported in Table 2. No systematic trend in  $R$  values for the salts studied has been observed. Since the best fit conductivity parameters are reproduced equally well over a wide range of arbitrarily chosen  $R$  values, a comprehensive correlation of the cosphere diameter of the studied systems could not be made in the present situation. This type of behavior has also been reported earlier.<sup>11,13,14</sup>

In both the mixed solvent media, the limiting ionic equivalent conductances decreases in the order:  $\lambda_{\text{Br}^-}^0 > \lambda_{\text{Na}^+}^0 > \lambda_{\text{Bu}_4\text{N}^+}^0 > \lambda_{\text{Ph}_4\text{B}^-}^0$  at each temperature indicating that the sizes of these ions as they exist in solutions follow the order:  $\text{Br}^- < \text{Na}^+ < \text{Bu}_4\text{N}^+ < \text{Ph}_4\text{B}^-$ . Another interesting observation is that the limiting ionic equivalent conductances of  $\text{Na}^+$  and  $\text{Br}^-$  ions decrease in going from 20 volume percent of acetonitrile to 40 volume percent of acetonitrile in the mixture at all temperatures investigated, whereas those for  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  ions exhibit an increase in going from 20 to 40 volume percent of acetonitrile in the mixture. This indicates that besides the relative permittivity and the viscosity of the media, specific interaction of the ions with the solvent media has a profound influence on their mobilities.

Although the association constants of the electrolytes do not vary significantly as a function of temperature, the limiting equivalent conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.

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**Table 1.** Derived Conductivity Parameters of Electrolytes in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

$T(\text{K})$	$\Lambda^0 (\text{S cm}^2 \text{ mol}^{-1})$	$K_{\Lambda} / (\text{dm}^3 \text{ mol}^{-1})$	$R / \Lambda^0$	$\sigma\%$ <sup>a</sup>
<b>20 Vol Percent of Acetonitrile</b>				
Bu <sub>4</sub> NBr				
308.15	125.96 ± 0.07	9.24 ± 0.04	16.47	0.05
313.15	135.50 ± 0.06	8.30 ± 0.03	14.77	0.03
318.15	149.27 ± 0.06	8.46 ± 0.03	14.85	0.03
NaPh <sub>4</sub> B				
308.15	84.16 ± 0.01	3.65 ± 0.01	11.24	0.02
313.15	94.05 ± 0.08	5.59 ± 0.08	12.11	0.03
318.15	102.92 ± 0.02	3.80 ± 0.02	11.50	0.03
NaBr				
308.15	152.27 ± 0.04	5.51 ± 0.01	10.76	0.02
313.15	164.80 ± 0.02	4.97 ± 0.01	10.20	0.01
318.15	179.96 ± 0.02	4.81 ± 0.01	10.07	0.01

Table 1. continued

Table 1. continued

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**40 Vol Percent of Acetonitrile****Bu<sub>4</sub>NBr**

308.15	117.52 ± 0.01	7.40 ± 0.01	12.11	0.01
313.15	128.59 ± 0.01	7.31 ± 0.01	11.97	0.01
318.15	137.35 ± 0.05	6.13 ± 0.02	11.09	0.03

**NaPh<sub>4</sub>B**

308.15	84.06 ± 0.06	3.64 ± 0.03	10.55	0.04
313.15	93.26 ± 0.04	3.29 ± 0.03	10.50	0.05
318.15	101.79 ± 0.06	2.38 ± 0.04	10.47	0.07

**NaBr**

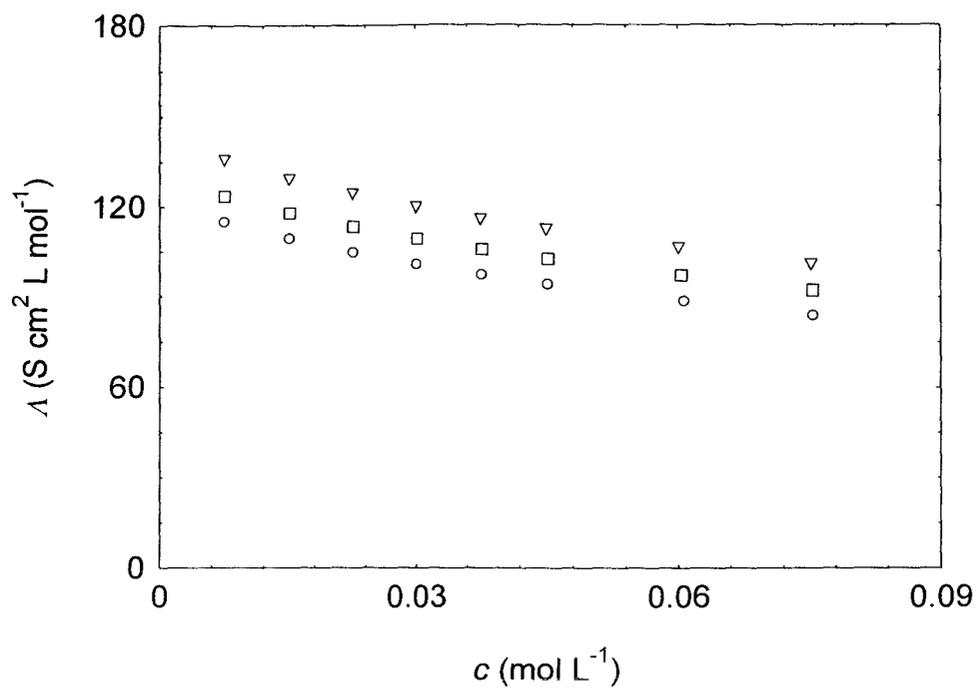
308.15	133.97 ± 0.07	1.92 ± 0.03	9.11	0.03
313.15	148.54 ± 0.08	2.29 ± 0.03	9.13	0.06
318.15	163.69 ± 0.10	2.27 ± 0.03	9.19	0.07

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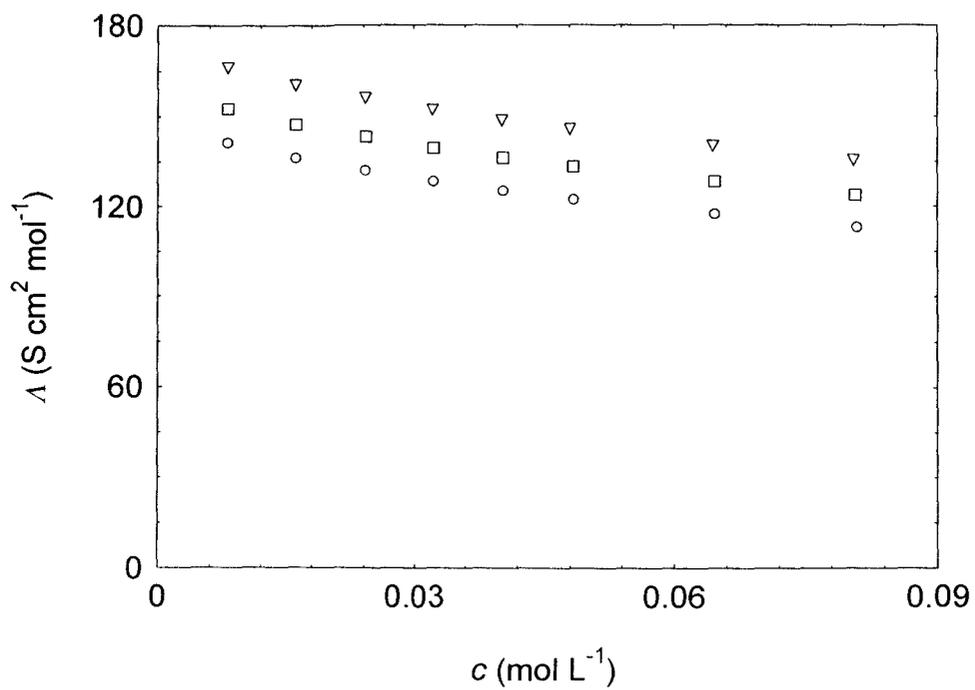
$${}^a \sigma \% = 100\sigma / A^0$$

**Table 2.** Limiting Ionic Conductances in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

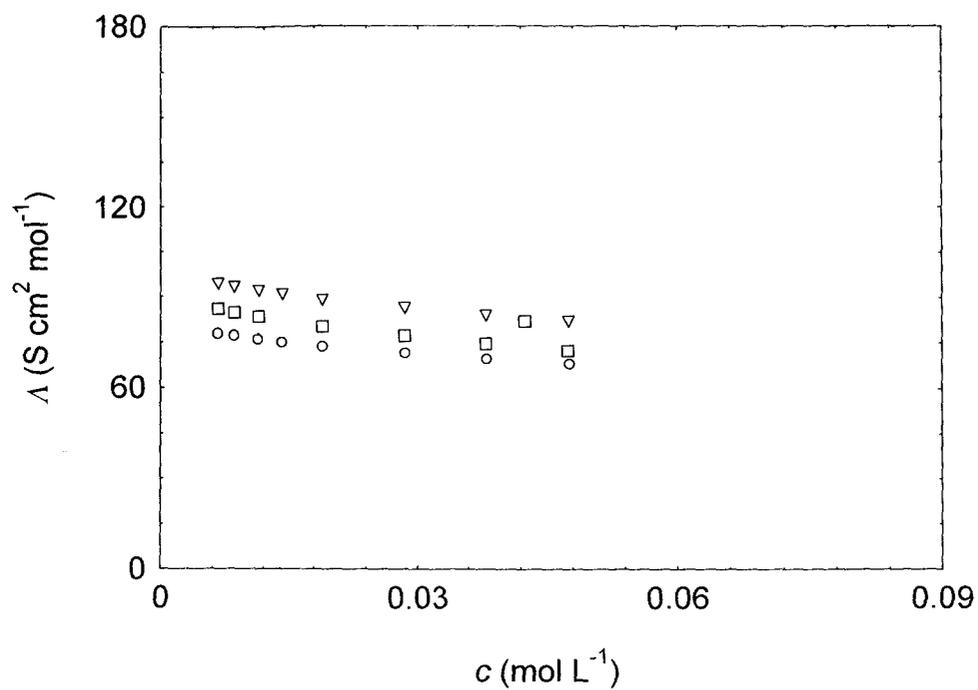
$T$ (K)	$\lambda_{\pm}^0$ (S cm <sup>2</sup> mol <sup>-1</sup> )			
	Na <sup>+</sup>	Bu <sub>4</sub> N <sup>+</sup>	Br <sup>-</sup>	Ph <sub>4</sub> B <sup>-</sup>
<b>20 Vol Percent of Acetonitrile</b>				
308.15	56.21	29.90	96.06	27.95
313.15	62.77	33.47	102.03	31.28
318.15	68.03	37.34	111.93	34.89
<b>40 Vol Percent of Acetonitrile</b>				
308.15	51.40	34.95	82.57	32.66
313.15	57.84	37.89	90.70	35.42
318.15	65.34	39.00	98.35	36.45



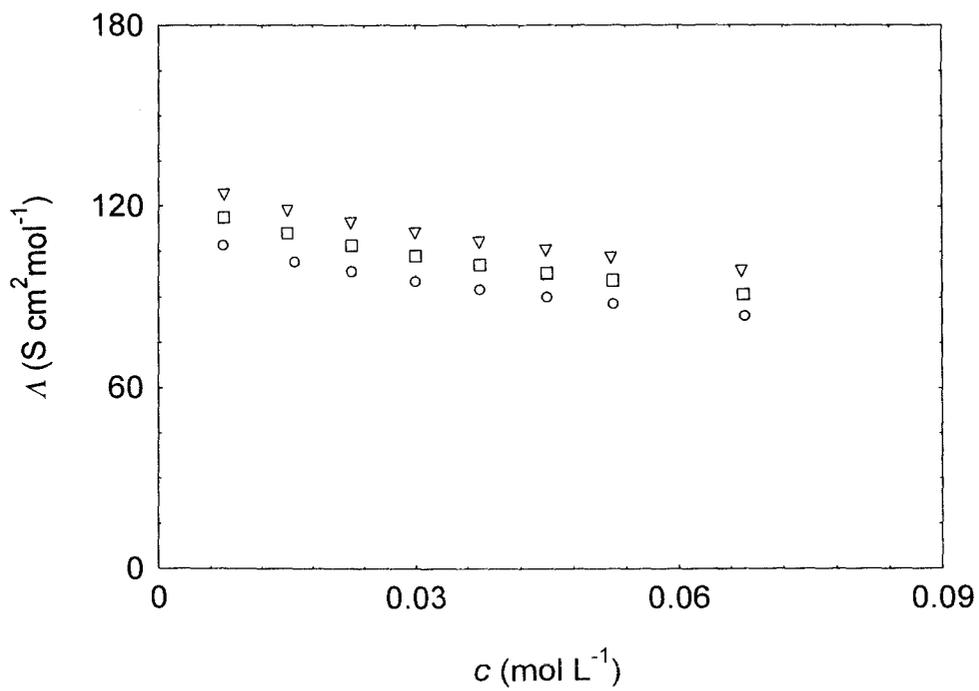
**Figure 1.** Concentration dependence of the equivalent conductance of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.



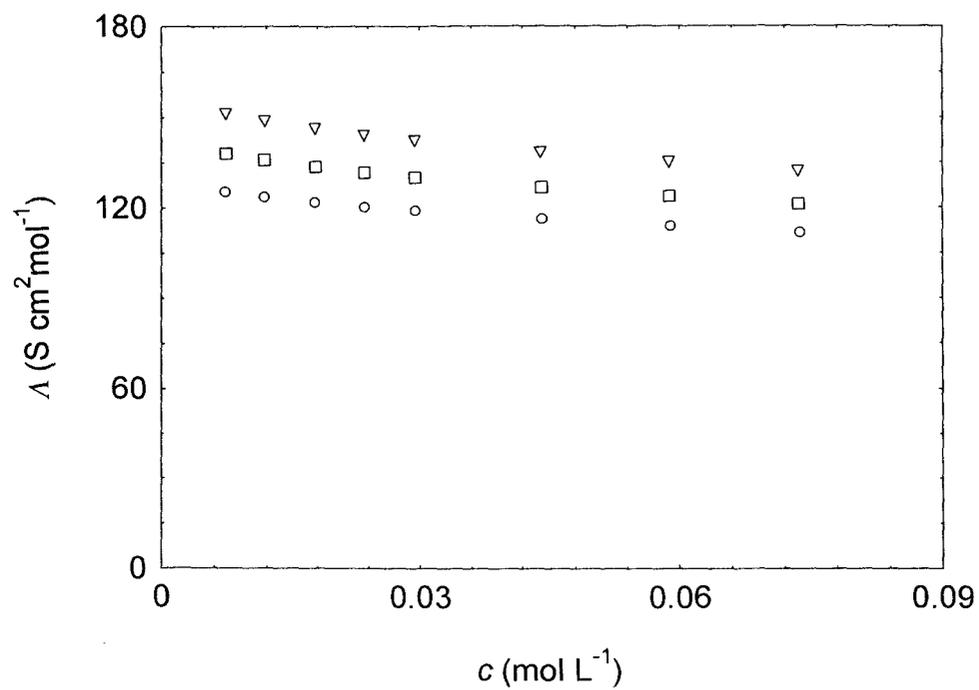
**Figure 2.** Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (◻) 313.15 K; (◂) 318.15 K.



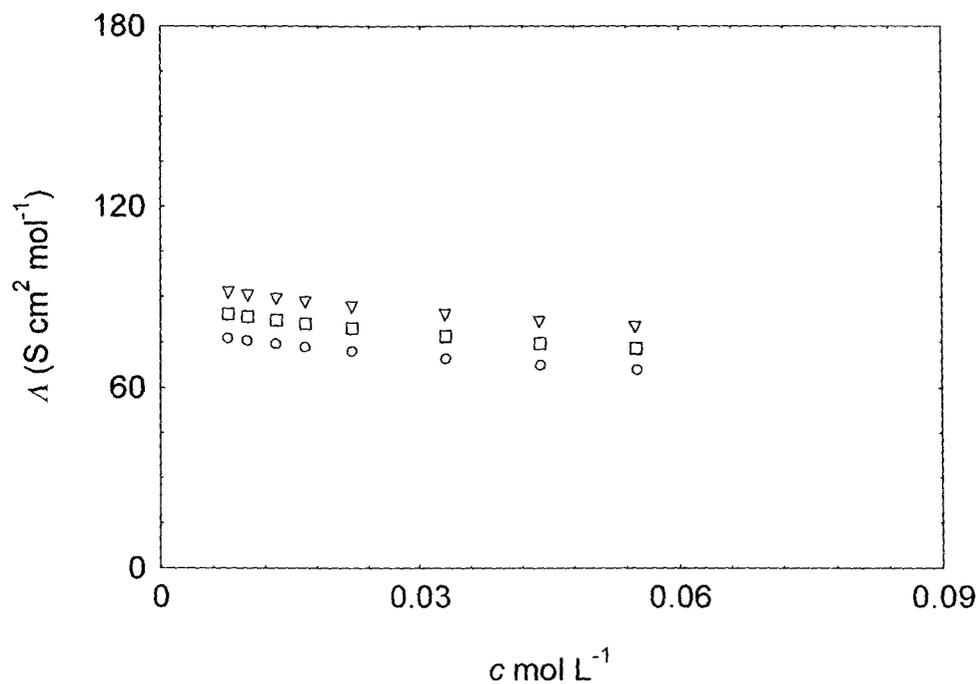
**Figure 3.** Concentration dependence of the equivalent conductance of sodium tetrphenylborate ( $\text{NaPh}_4\text{B}$ ) in 20 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.



**Figure 4.** Concentration dependence of the equivalent conductance of tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.



**Figure 5.** Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (◻) 313.15 K; (◂) 318.15 K.



**Figure 6.** Concentration dependence of the equivalent conductance of sodium tetrphenylborate ( $\text{NaPh}_4\text{B}$ ) in 40 volume percent acetonitrile-water mixture at different temperatures: (○) 308.15 K; (□) 313.15 K; (▽) 318.15 K.

## Publications

### List of Papers Published

1. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15K , D. Ghosh and B. Das, *J. Chem. Eng. Data*, **49**, 1771 (2004).
2. Electrical Conductivity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media: Experiment and Data Analysis Using the Manning Counterion Condensation Model and the Scaling Theory Approach, D. Ghosh, A. Bhattarai, and B. Das, *Colloid Polym. Sci.*, 287,1005 (2009).

**Addendum / Corrigendum in the Thesis entitled "Studies on the Behaviour of Polyelectrolytes & their Interaction with Small Ion and Surfactant in Mixed Solvent" Submitted by Sri Debapratim Ghosh, M.Sc. of the Department of Chemistry, University of North Bengal, Darjeeling 734 013, India for the Degree of Doctor of Philosophy (Science) of the University of North Bengal**

**A. General Observations:**

1. Chapter I presents a brief account of the works done in this dissertation while Chapter II provides an in-depth introduction and informative review of the subject matter of the thesis. Chapter IV describes a study on the conductivities of sodium polystyrenesulfonate (NaPSS) in salt-free acetonitrile-water mixed solvent media and their *quantitative* description by the present-day available model for semidilute polyelectrolyte conductivity, whereas Chapter V presents an analysis of the conductivity of NaPSS-NaCl-acetonitrile-water system on the basis of the so-called "*phenomenological*" approach to provide *qualitative* guidelines to the polyion-counterion interactions in presence of a salt. Chapter VI employs the method of *isoionic dilution* to maintain the intermolecular interactions at a constant level for the determination of the intrinsic viscosity of NaPSS, whilst Chapter VII revealed how the intermolecular interactions could be eliminated completely by adding an excess of an electrolyte to allow the determination of intrinsic viscosities. For better clarity of presentations, the pair of chapters (I and II), (IV and V), and (VI, VII) have been presented separately since each one of a pair deals with different aspects. The chapters have been written as self-sufficient articles maintaining at the same time their federal existence in the dissertation and, that is why each has its own experimental section. Analyses of the conductivity data of the NaPSS in absence and in the presence of a salt (*cf.* Chapters IV and V) require information on the limiting ionic equivalent conductances of the counterion in acetonitrile-water mixtures and the latter have been obtained from a separate measurement of the electrical conductances of appropriate salts in acetonitrile-water mixtures and analysis using suitable equations applicable for salt solutions (Annexure I). Since the present dissertation deals with the behaviour of polyelectrolytes, studies on the electrical conductances of salts in acetonitrile-water mixtures have been reported separately as an annexure so that it would not hamper the spirit and the continuity of the results presented for the polyelectrolyte system under investigation.
2. Equivalent conductivities of salt-free NaPSS in water have been referred to and compared with the data presented here in the mixed solvent media (*cf.* page 61, lines 9-16). The conductivity results with the same molecular weight of NaPSS as that used within the premises of the present dissertation are not, however, available in the literature in aqueous NaCl solutions. Moreover, the viscosity and density data with appropriate molecular weight of NaPSS are also not available in the literature in aqueous or in brine solutions. The available values of the *cmc*s of aqueous CTAB have been shown (page 144, lines 1-2) and due reference has been made to the literature sources.

3. In Chapters VI and VII, all basic viscosity data (from which all other parameters were evaluated) have been shown in the Figures.
4. All information on the molecular interactions obtained from the variations of the Huggins constants has been reported in the text of Chapter IX (page 100, lines 24-26; page 101, lines 2-5; page 101, lines 15-17) based on the concept described in the literature (reference 19 of Chapter IX).

#### B. Some Critical Comments:

1. There have been some inadvertent mistakes in the dissertation. The precisions of the temperature and density measurements would be one order of magnitude higher than those reported. The precision of the viscosity measurements was always within two percent. Although the viscosity values are, in a large number of cases, reported upto three decimal places, studies reporting the viscosity values upto four decimal places are not uncommon [e.g., *Z. Phys. Chem.*, **138**, 185 (1983); *J. Chem. Soc., Faraday Trans. 1*, **84**, 3877 (1988); *J. Chem. Soc., Faraday Trans. 1*, **85**, 4227 (1989); *J. Chem. Soc., Faraday Trans. 1*, **86**, 2225 (1990); *J. Chem. Eng. Data*, **44**, 6 (1999)].
2. Page 67, Table 1: The large departure of the experimental equivalent conductances from those calculated according to the Manning model is amply signified by the very high values of the standard deviations reported within the parentheses.
3. The *cmc* values of CTAB in acetonitrile-water systems have not been reported earlier and hence a comparison of the values reported here with the literature values is not possible. It may be noted that the *cmc* values obtained in the present study have been reported upto two decimal places (*cf.* page 150, Chapter IX, Table 1). The *cmc* values (reported upto three decimal places) shown in line 1 of page 144 are those taken from the literature (the value of 1.0900 should be read as 1.090; it has been a typographical error) [reference 11 of Chapter IX]. The effect of the presence of acetonitrile in water and its role in the process of aggregation of CTAB induced by NaPSS in mixed solvents has been described at length (page 146, lines 16-28).

*Debapratim Ghosh*  
(Debapratim Ghosh)

Place: North Bengal University

Date: March 23, 2012

*Bijan Das*  
(Bijan Das)

Supervisor

PROFESSOR OF CHEMISTRY  
University of North Bengal

