

Solution Properties of Sodium Polystyrene Sulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

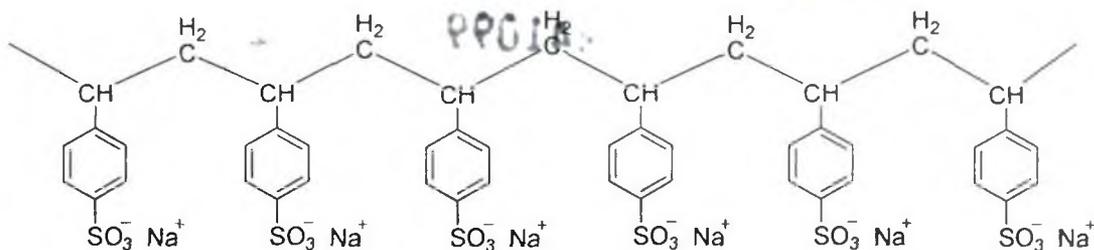
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By

Ranjit De, M. Sc.



DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NORTH BENGAL

DARJEELING 734 013, INDIA

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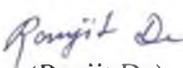
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Department of Chemistry
University of North Bengal
Darjeeling 734 013


(Ranjit De)

Solution Properties of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

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Preface

Scope and Object of the Work

Since the emergence of polymer science, polyelectrolytes have been the subject of extensive investigation. These 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 polyelectrolytes stems from the scientific curiosity in understanding their behaviour and also from their enormous potential in commercial applications. Polyelectrolytes have been utilized to assemble nanostructured materials with desired properties. Potential applications in medicine and biomedical engineering are also being extensively pursued. Complexes of polyelectrolytes with such conjugated polymers as polythiophenes and polyanilines are being used commercially as conducting coatings. These are extensively 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.

Physicochemical properties of polyelectrolyte solutions have been studied for several decades, but several of them have not yet found a satisfactory theoretical interpretation. In many cases though a qualitative understanding is available, a quantitative understanding is still awaited. For others, the origin of the phenomena observed remains partly obscure, indicating that the current treatment of the polyelectrolyte behaviour is incomplete and that more 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 present situation is far from satisfactory.

In recent years, there has been an upsurge of interest in the study of polyelectrolytes stimulated by the availability of sophisticated 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.¹⁻⁷ This is partly because many polyelectrolytes, usually with high charge densities, are difficult to dissolve in solvents other than 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.⁷⁻¹⁰

The principal 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 intimately related with the expansibility of the polymer chains, whereas the second is not only manifested in counterion binding but also in the extent of solvation and the solvent structure in the vicinity of polyelectrolytes. Both of these factors are, in turn, related to the relative permittivity of the solvent media. Use of a series of mixed solvents corresponds to a systematic variation in the relative permittivity of the media and hence provides us an opportunity 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 polystyrenesulphonate) in 2-ethoxyethanol–water mixed solvent media using three different experimental techniques namely, electrical conductivity, viscosity and density.

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Chapter 1

Summary of the Works Done

The present dissertation addresses the issue of various types of interactions prevailing in solutions of a polyelectrolyte – sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media using three well-established experimental techniques.

Sodium polystyrenesulphonate is an important industrial polymer with a wide range of applications, for example it is used 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 etc.¹⁻⁴ The present study is, therefore, expected to help extend the fruitful use of this polymer.

This dissertation has been divided into ten chapters.

Chapter 1 (the present chapter) gives a brief account of the works done in this dissertation.

Chapter 2 forms the background of the present work. After presenting a brief review of the notable works in the field of polyelectrolyte solution chemistry, properties like conductance, viscosity and partial molar volumes have been discussed in details. The importance and utility of different methods in order to probe the polyion-counterion 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 3 describes the experimental techniques used to obtain the results presented in the dissertation.

Chapter 4 reports the electrical conductivities of solutions of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixed solvent media within the temperature range 308.15 – 313.15 K in absence of an added salt. The applicability of the Manning theory⁵ for conductivity of salt-free polyelectrolyte solutions is examined and a major discrepancy against this 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.

Chapter 5 describes the application of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et al.*⁶ using the scaling theory approach to the experimental results of electrical conductivity of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures. We have been able to quantitatively describe the electrical conductivity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions.

In Chapter 6, the electrical conductivities of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media within the temperature range 318.15 – 323.15 K in presence of sodium chloride have been reported. The conductance data have been analyzed on the basis of an equation developed in this study following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a semidilute polyion chain according to Dobrynin *et al.*⁷ Excellent quantitative agreement between the experimental results and those using the equation developed was observed.

Intrinsic viscosities of sodium polystyrenesulphonate in water and in 2-ethoxyethanol–water mixed solvent media within the temperature range 308.15 – 323.15 K obtained using the isoionic dilution technique have been reported in Chapter 7. 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 operative in the polyelectrolyte solution under investigation.

Chapter 8 reports the viscosities of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media both in absence and in presence of NaCl with varying concentrations within the temperature range 308.15 – 323.15 K. 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.

Chapter 9 describes the apparent molar volumes of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media within the temperature range 318.15 – 323.15 K. This study indicates that in 2-ethoxyethanol–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. A delicate balance of the influences of the volumetric terms, namely the void-space partial molar volume (\bar{V}_{str}^0), the

electrostriction partial molar volume (\bar{V}_{elec}^0) and the caged partial molar volume (\bar{V}_{cage}^0) is found to control the volumetric behaviour of this polyelectrolyte in 2-ethoxyethanol–water mixed solvent media. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

The dissertation ends with some concluding remarks in Chapter 10.

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Chapter 2

Introduction

2.1 Definition of Polyelectrolytes

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

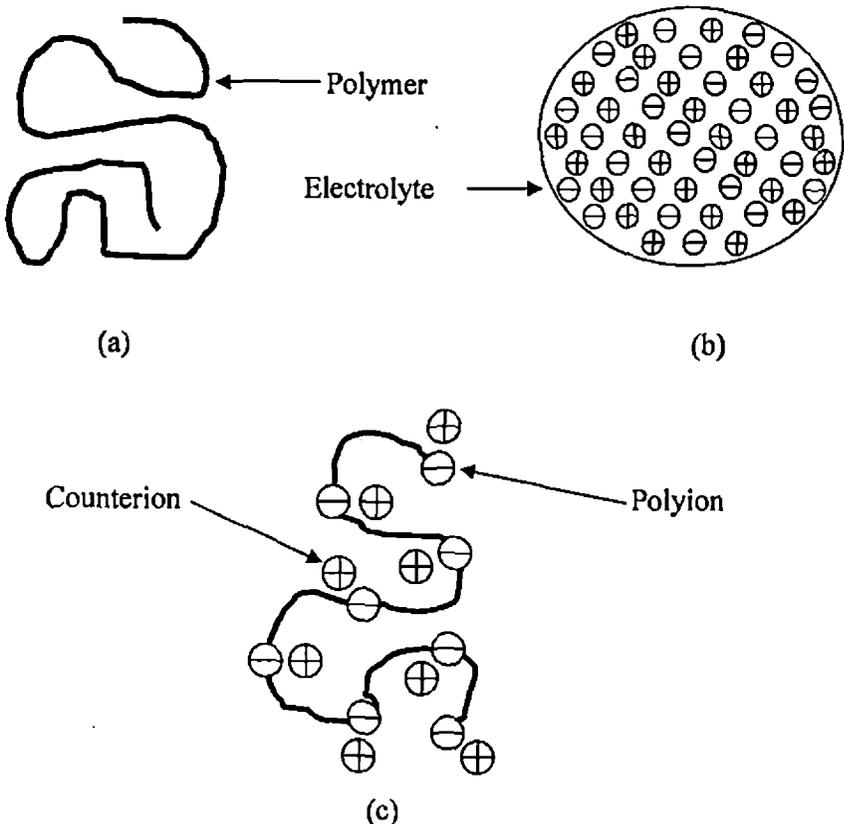


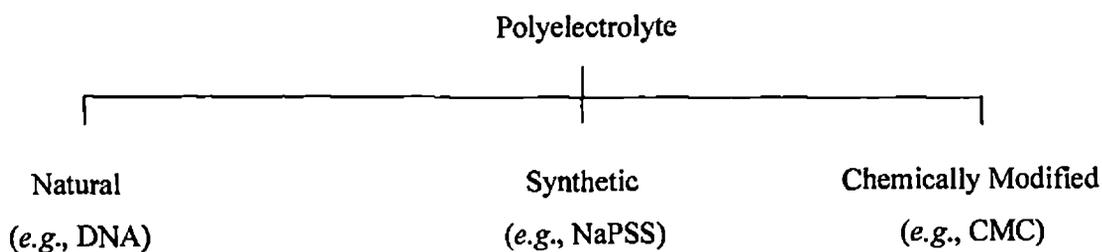
Figure 2.1 (a) Polymer, (b) Electrolyte, and (c) Polyelectrolyte

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

The electrostatic interactions between the charges on the polyion chain and those between the polyion and the surrounding counterions play very important roles in determining the behaviour of polyelectrolytes in solution, which are quite distinct from that of the non-polyelectrolytes. The conformations of polyelectrolytes in dilute solutions depend on the fraction of charged groups on the polyions and the ionic strength of the solution. For weakly charged polyelectrolytes (or macromolecules carrying a small percentage of ionizable groups) the interplay between the non-Coulombic interactions such as van der Waals interaction, hydrogen bonding and other molecular interactions play an important role in governing their conformations. The behaviour of polyelectrolytes is also influenced by such factors as the solution pH , nature of the ions, molecular weight, solvent polarity, dielectric constant, temperature etc. Moreover the presence of multivalent counterions significantly influences the structure and dynamics of polyelectrolyte solutions.

2.2 Classification of Polyelectrolytes

There are different ways of classification of polyelectrolytes. It is possible to distinguish between natural, synthetic and chemically modified natural polyelectrolytes. Examples are deoxyribonucleic acid (DNA), sodium polystyrenesulphonate (NaPSS) and carboxymethylcellulose (CMC), respectively.



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

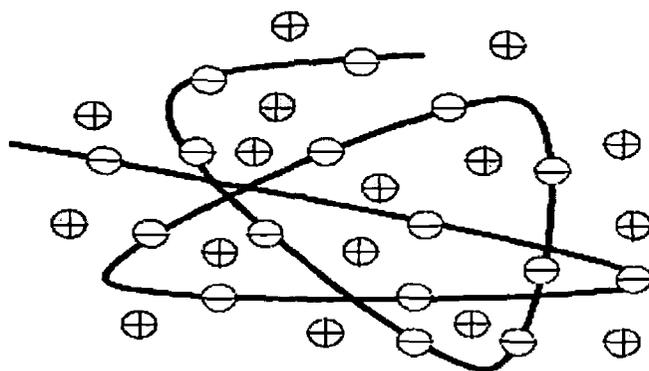
groups are all anionic, cationic or a mixture of both. Another distinction is also possible between strong polyelectrolytes (e.g., sodium polystyrenesulphonate), which acquire spontaneously full charge, and weak polyelectrolytes (e.g., polyacrylic acid) which are only partially charged upon dissolving.

Based upon the molecular architecture, polyelectrolytes have been divided into two important categories namely linear and branched polyelectrolytes. In linear polyelectrolytes, a large number of atoms are connected together to form the backbone chain. Although in a topological sense the backbone is linear, the shape of the polymer might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.¹ Branched polyelectrolytes, on the other hand, do not have linear chains and are less investigated species compared to their linear analogues.²⁻⁷ The different known branched structures are comb-like, stars (regular and irregular), H-shaped, super H-shaped polymer and dendrimers.^{3,8-13}

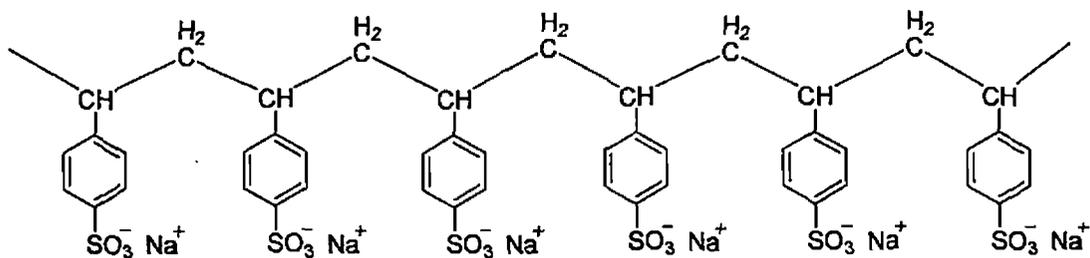
Polyelectrolytes could also be distinguished depending upon their conformations. Flexible polyelectrolytes (Figure 2.2a) bear a macroion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions.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

2.3 Importance of Polyelectrolytes

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

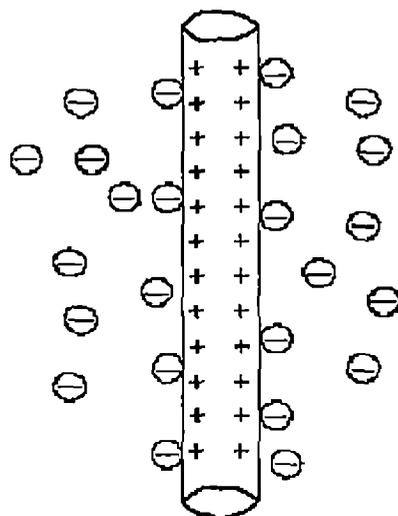


(a)

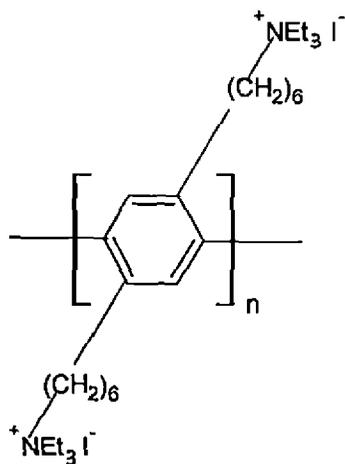


(b)

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



(a)



(b)

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

Synthetic polyelectrolytes have been a very active area of scientific research and commercial growth. Conformations of the polyelectrolytes as well as the interactions prevailing in these systems can be controlled by varying one or more of the parameters thus making such systems not only an interesting and rich area for exploration of novel phenomena but also an area of research which could open up new possibilities of applications in variety of fields. Water soluble polyelectrolytes have found application in biochemical and medical research and deveopment. There is presently much research in using biocompatible polyelectrolytes for implant coatings, for controlled drug release, and other applications. Current applications of polyelectrolytes are also in the areas of ion exchange resins, waste water treatment, oil-spill treatment, ion and gas selective membranes for fuel cells, polymeric surfactants, personal care products, cosmetics, soaps, shampoos, pharmaceuticals, biosensors, absorbents, etc. Potential applications in medicine and biomedical engineering are also being extensively pursued.

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

Table 2.1 Application of Some Natural Polyelectrolytes

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

Table 2.2 Application of Some Synthetic Polyelectrolytes

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

2.4. Concentration Regimes in Polyelectrolyte Solutions

The different properties of polyelectrolytes in solutions are very much dependent upon their concentrations in solutions. The three different concentration regimes in polyelectrolyte solutions, namely dilute, semidilute and concentrated regions, could be understood from the concept of overlap concentration which is defined as the concentration at which the polymer chains start to interact with each other *i.e.*, start to overlap. It is generally expressed as c^* ($=1/N_A L^2 a$ where N_A = Avogadro number, L = contour length and a = length of a monomer unit). A dilute polymer solution, on the other hand, refers to the concentration region where the polymer chains are isolated and do not interact with the other chains. Here the polymer concentration is less than the overlap concentration, c^* . In dilute solutions, polyelectrolytes have a large overall size and a rather stiff local conformation.¹⁴ In the dilute regime, the chain is represented by an extended rod-like configuration of N_D electrostatic blobs of size D . Each of them, containing g_e monomers, bears a charge of $q_D = z_c f e g_e$, with z_c being the counterion valence, e the electronic charge, and f the fraction of ionized charged groups on the polyion chain (and consequently, the fraction of uncondensed counterions). With increasing polyelectrolyte concentration, the chains become more flexible. When the polyelectrolyte concentration exceeds the overlap concentration c^* , the chains start to overlap and the conformations of the single chains are greatly modified. This region is commonly referred to as the semidilute regime. In semidilute solutions, the polyion chain is modelled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bear an electric charge of $q_\xi = z_c f e g$.

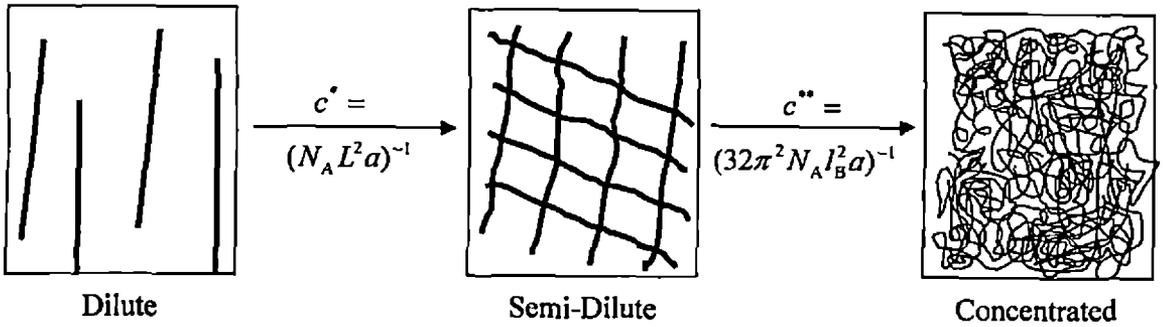


Figure 2.4 Concentration regime of polyelectrolyte solution

Because of the strong electrostatic interactions within each correlation blob, the chain is in fully extended conformation of electrostatic blobs in the semidilute-unentangled regime ($c^* < c < c_e$). At higher concentrations where $c > c_e$, significant overlap of neighbouring chains occurs, and this strongly affects the chain motion (semidilute-entangled regime). At even higher concentrations, the electrostatic blobs begin to overlap, and owing to the increase of electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments¹⁵ suggest polyelectrolyte behaviour similar to that of a neutral polymer solution. Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration c^* , at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length (*i.e.*, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the stand of N/g beads of size ξ_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.¹⁶ This evidence mostly stems from the study of non-equilibrium properties, such as viscosity, conductance, or diffusion. Experiments below the overlap concentration c^* are difficult to perform because of the very low concentrations and subsequently very low effects to be monitored, requiring extreme experimental sensitivity. Measurements above c_D also might be problematic, arising from the high solution viscosity. It is, therefore, not surprising

that most of the experimental results described in the literature seem limited to the concentration region between c' and c_p . To arrive at the final conclusions as to the existence of these and other possible concentration regimes, more extensive experimental investigations and further theoretical efforts are required.

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

Despite the increasing theoretical and experimental efforts over the last 8-9 decades, the solution properties of polyelectrolytes are not yet well understood. Extensive reviews and entire books have been devoted to the properties of polyelectrolyte solutions¹⁶⁻³² and no attempt is, therefore, made here to provide a comprehensive review of the vast literature which exists on these subjects. In what follows, we will highlight some of the important applications of different experimental techniques to polyelectrolyte solutions with particular reference to various aspects of some of the transport and thermodynamic properties of polyelectrolyte solutions as the present dissertation is concerned with such studies of polyelectrolyte solutions.

Early studies on the synthetic polyelectrolytes have been reported in the 1930s.³³⁻⁴⁰ 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.⁴¹ At the same time Kagawa in Nagoya, Japan also started an independent program on polyelectrolytes. In his first paper on polyelectrolytes, Kagawa⁴² introduced counterion binding as an important concept in understanding the characteristic physicochemical properties of polyelectrolytes, e.g., counterion activity and the dissociation constant.

Since the outset of polyelectrolyte research, electrochemical methods have been used as powerful tools to investigate and analyze the equilibrium properties as well as the transport phenomena.^{16,24,31,43} 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.^{16,19,24,25,31,43} 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.^{2,31}

The solvodynamic behaviour of polyelectrolyte molecules depends on their mass as well as on their size and shape, both modified by interaction with the third component, for example the salt, which influences the conformation of the macroion. Besides the scattering methods (discussed later), viscometry offers the possibility of studying conformational changes of polyelectrolytes, in particular, the influence of the ionic strength on the molecular dimension (please see later).

Viscosity is clearly a property of the solution as a whole under the influence of a mechanical perturbation. Diffusion phenomena, on the other hand, are directly related to the relative motion of solute particles in a stationary system. Various kinds of isothermal diffusion may be distinguished, which refer to different motions and are observed under different experimental conditions. For instance, the random motion of particles in a homogeneous system at thermodynamic equilibrium is responsible for density or concentration fluctuations. These motions are investigated by dynamic light scattering. On the other hand, diffusional fluxes arise in systems in which macroscopic chemical potential gradients exist for one or several thermodynamic species. An intermediate situation corresponds to the setup for self-diffusion measurement with fluxes of labelled molecules in a system containing a chemically identical species of different isotopic composition. All kinds of different diffusion measurements have been performed on polyelectrolyte solutions.² 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.^{2,16}

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.⁴⁴ However, at sufficiently high amounts of supporting low molar mass electrolytes, the motion of the polyions and the counterions is largely decoupled and ultracentrifugation is a powerful tool for molecular mass determination. Additionally, the conformational changes of the polyions with varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional

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coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.^{2,45,46}

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.^{2,19} 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.^{2,47-50}

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.² 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.^{2,16,51-56} 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^{55,56} and the results indicated failure of the Manning and the Poisson-Boltzmann cell models. Later, Deserno *et al.*⁵⁷ 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.³¹

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.^{32,58-61} For the past five decades there has been an increasing interest in dynamic scattering methods, particularly dynamic light scattering (DLS), because these could provide important insight into the dynamics of polyelectrolyte solutions to very high concentration, and these are also capable of providing useful structural information, e.g., translational diffusion coefficient and solvodynamic radius of the scattering species.

In particular, the main interest of light scattering studies on polyelectrolyte solutions was focused up to about 1980 on the investigation of coil expansion and the second virial coefficient in relation to the ionic strength of the medium, besides their function as routine method in determining the mass average molecular mass.⁶²⁻⁶⁶ 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.^{64,67,68} 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.⁶⁹⁻⁷² 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.^{73,74}

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.⁷⁵⁻⁸²

Despite the variety of conformational effects that may be studied by DLS in salt-containing polyelectrolyte solutions, large number of studies have been devoted to fundamental problems of the structures of polyelectrolyte solutions at low ionic strength, and their dependence on polymer concentration, ionic strength, and molecular mass.^{2,83-85}

It may be pointed out that the experimental data obtained from different scattering methods as to the intermolecular structure factor of semidilute salt-free polyelectrolyte solutions are qualitatively in good agreement, but quantitative discrepancies occur and the real structure models are not clear at present. Comprehensive and sophisticated experiments

are necessary to test the theoretical models in more details. A brief and very useful review on the application of these different scattering techniques is available in Dautzenberg *et al.*²

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 counterions⁸⁶⁻⁹³ despite the fact that the use of a series of mixed solvents permits alteration of the relative permittivity of the media in a systematic manner thus enabling one to study the varying polyelectrolyte behaviour in general. Studies in such systems, could provide important information on the interactions between the polyions and the counterions and also on the conformation of the polyions in solution, from a more general point of view.

Here, we shall particularly dwell upon different aspects of transport and thermodynamic properties of polyelectrolytes, as the present dissertation is intimately related to the studies of electrical conductances, viscosities, and partial molar volumes of sodium polystyrenesulphonate, an anionic polyelectrolyte, in 2-ethoxyethanol–water mixed solvent media. The effects of added salt and temperature have also been investigated.

2.6 Some Important Properties of Polyelectrolyte Solutions

2.6.1 Polyelectrolyte Conductance

2.6.1.1 Manning Model for the Conductance of Salt-Free Polyelectrolyte Solutions^{19,94-98}

The specific conductance and the equivalent conductivity, Λ , are two experimentally determined parameters which are suitable to describe the electrical transport properties of polyelectrolyte solutions because they take into account the movement of any charged entity present in the system under the influence of an externally applied electric field. The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory^{19,94-98} for dilute solutions of infinitely long linear polyionic chains.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by a linear charge density parameter defined by^{19,96,98}

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

where e is the protonic charge, D the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzmann constant

and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense onto the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law of the equivalent conductivity for a salt-free polyelectrolyte solution is related to ξ by the following equation^{95,96}

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

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is the polyion-counterion interaction parameter given by^{19,96,98}

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

In contrast to Huizenga⁹⁹ 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, λ_p has been derived theoretically for the cylinder model of polyelectrolyte,⁹⁷ and it follows for counterions with a charge of z_c

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

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

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

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

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

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

2.6.1.2 Limitation of the Manning Model

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

A survey of the literature indicated that although in a limited concentration range, the variation of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not generally agree with the predictions. This aspect has been amply described in the reviews by Bordi *et al.*³¹ and Wandrey and Hunkeler⁴³ 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 presented⁹⁶ 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 Hayes¹⁰⁰ and Szymczak *et al.*¹⁰¹ 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 Hayes¹⁰⁰ studied the electrical conductances of lithium, sodium, potassium, cesium, magnesium, calcium, and strontium salts of polystyrenesulphonic acid covering the dilute and semidilute regimes (*i.e.*, above and below the overlap concentration, c^*) at 298.15 K. They observed a minimum in the equivalent conductivity in the range 7×10^{-3} to 1×10^{-2} monomol·L⁻¹ for all counterions and the two investigated polyelectrolytes of molar masses of 70000 and 500000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the increase after the minimum was passed could not be explained. It was concluded that the applicability of the Manning theory is questionable for a concentration range where chain coiling is probable. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulphonic acid in semidilute solutions were carried out by

Szymczak *et al.* at 298.15 K.¹⁰¹ 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.*^{102,103} dealt with alkali metal salts of a number of ionic polysaccharides (carboxymethylcellulose, polypectate, dextran sulfate). These authors concluded from the comparison of the various polyions bearing different charge density parameters that, although qualitative agreement is obtained with the Manning limiting law, the concentration dependence predicted is in agreement with the experimental curves only for the polyions with a relatively low charge density. The behaviour of dextran sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rod-like structure of the polyion on which the theory is based.

Significant deviations of the experimental equivalent conductivities of sodium and potassium dextran sulfate from the Manning predictions in the semidilute concentration regime were also reported by Beyer and Nordmeier.¹⁰⁴

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.⁹²

Wandrey *et al.*¹⁰⁵ 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.*⁹³ compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4000 and 167000 for both the dilute and semidilute regimes. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polymer molecular weight. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molecular weight sample is hardly surprising, since these data are all above c^* , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molecular weight sample is noteworthy since these data are all below c^* .

In a study on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-*co*-(vinyl pyrrolidone)], Rios¹⁰⁶ confined the attention below the overlap concentration. Whereas the Manning model predicts a slow but monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration, a maximum was observed experimentally in each of these three cases. Although, the agreement between the

experiment and theory is generally poor, theoretical curves approach the experimental ones for the lithium and sodium salts over a very narrow concentration range for very dilute solutions.

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

2.6.1.3 Scaling Theory Approach for the Conductance of Salt-Free Polyelectrolyte Solutions¹⁰⁷

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

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

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

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

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

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

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

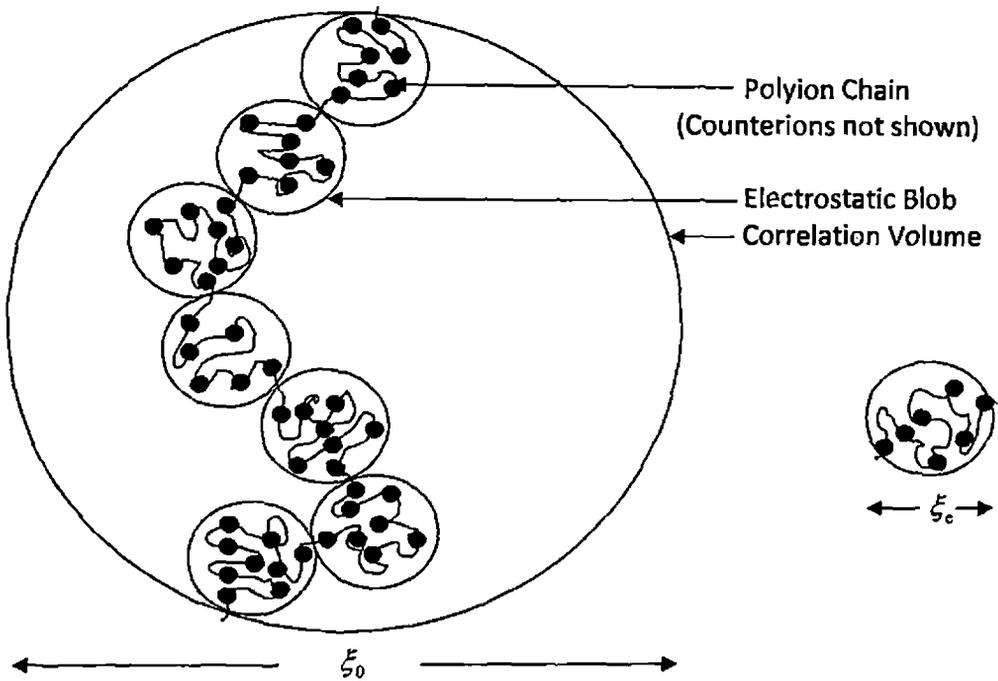


Figure 2.5 Schematic representation of correlation volume in a semidilute polyelectrolyte solution

The equivalent conductivity of a polyelectrolyte solution is then given by

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

The above expression given by Colby *et al.*¹⁰⁷ is derived taking into account the scaling arguments proposed by Dobrynin *et al.*¹⁰⁸ neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. As can be seen the above model has a single free parameter f , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge-density parameter (ξ), 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^{31,93,107} and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify different concentration regimes with varying fractions of uncondensed counterions.¹⁰⁹ 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.¹¹⁰

2.6.1.4 Effect of Salts on the Conductance of Polyelectrolyte Solutions

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

Although the polyelectrolyte conductivities have been well-understood in salt-free solutions¹⁰⁷ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*,¹⁰⁸ the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning¹¹⁰ first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory⁹⁵ without much success. In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the "primitive additivity") of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.^{7-9,111,112}

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

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

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

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

Ander *et al.*^{111,112} modified the “primitive” additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte–salt solution as

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

where D_2 and D_2^0 are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion co-efficients D_2/D_2^0 has been used as a quantitative measure⁹⁵ of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s(D_2/D_2^0)$.

Although the “modified” additivity has been shown to be somewhat better than the “primitive” one, departures from the experimental results are still prominent.¹¹¹⁻¹¹⁵ Later Bodri *et al.*¹¹⁶ evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach¹⁰⁸ and compared them with the experimentally determined values. The agreement was rather good, although a quantitative description was not achieved.

Very recently, a simple approach has been put forward by us¹¹⁷ to analyze the conductivity of polyelectrolyte solutions in the presence of an added electrolyte following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*¹⁰⁷ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*¹⁰⁸

Following Colby *et al.*,¹⁰⁷ the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

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

where c is the number density of monomers, λ_c^0 the limiting equivalent conductivity of the counterions, the η_0 the coefficient of viscosity of the medium.

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

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

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

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

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

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

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

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

2.6.2 Polyelectrolyte Viscosity

2.6.2.1 Viscosity of Polyelectrolytes as a Function of Concentration

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

reduced viscosity η_{sp}/c_p (defined as $\eta_{sp}/c_p = (\eta - \eta_0)/\eta_0 c_p$, where η is the viscosity of the solution, η_0 is the viscosity of the solvent in the absence of polymer and c_p is the (monomer) concentration of the polymer solution) is proportional to c_p . This well-known relation is used for determining the intrinsic viscosity $[\eta]$ simply by extrapolation of η_{sp}/c_p values to $c_p = 0$. On the other hand, salt-free polyelectrolyte solutions exhibit an anomalous concentration dependence of viscosity. Early investigations of the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that reduced viscosity would increase without bound as one lowers the polymer concentration. In these studies, which are summarized in the pioneering work of Fuoss,^{119,120} a straight line is obtained when the reciprocal of the reduced viscosity is plotted as a function of the square root of the polymer concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the reciprocal of the intrinsic viscosity. However, careful investigation of the dilute solution behaviour revealed that the apparently unbounded increase of the reduced viscosity is invariably followed by a maximum,¹²¹⁻¹²⁴ and that normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. Thus, the method of Fuoss could not be used to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. It has been argued that the observed behaviour is a consequence of screening of long-range intermolecular interactions by the residual electrolyte in the solution, an explanation supported by the observation of "regular" neutral polymer behaviour upon isoionic dilution of polyelectrolyte solutions.¹²⁴ The anomalous shape of the curve of the reduced viscosity versus concentration for dilute salt-free solutions, found in many studies during the last five decades, was generally interpreted as the result of expansion and shrinking of the flexible macroion due to short-range interactions. Most of these investigations were performed on weak polyelectrolyte systems *e.g.*, derivatives of polyvinylpyridine and polymers containing carboxylic acids, as reviewed by Tanford.¹²⁵ Hodgson and Amis^{126,127} 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,^{128,129} poly (galacturonic acid) and its sodium salt,¹³⁰ sodium

polystyrenesulphonate,^{122,131} sodium carboxymethylcellulose,¹³² polysulphobetaines,¹³³⁻¹³⁶ polyelectrolytes with poly(*p*-phenylene) backbone¹³⁷ 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.¹³⁸ Later Cohen *et al.*^{122,123} derived a similar relation on the basis of the theory by Hess and Klein¹³⁹ and have shown that the relation derived fits well the experimental results with some adjustable parameters. Both of these approaches are characterized by assumptions that viscosity is dominated by intermolecular interactions which are primarily electrostatic in nature and by the treatment of the solution as a simple viscoelastic liquid. However, in spite of the success of these treatments to a limited number of systems, the assumptions underlying these approaches are questionable.

Another interesting approach to the viscosity problem has been presented by Nishida *et al.*¹⁴⁰ who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.¹⁴¹ The interaction between the particles is described by a Debye-Hückel potential which exhibits a maximum as a function of polyion concentration. The maximum in the interaction energy is manifested by the maximum of the viscosity. The calculation may be employed to separate formally the influence of electrostatic interaction and of conformational change of the polyion on experimental viscosity data.

In their approach Nishida *et al.*¹⁴⁰ 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.*¹⁴² demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.¹³⁹ On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following equation,

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

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

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

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

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

when λ is >1 or ≤ 1 , respectively.

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

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

in which $(\eta_{sp} / c_p)_{HK}$ represents the electrostatic contribution expressed in Eq. (15). Besides describing the polyelectrolyte concentration dependence of the reduced viscosity, Eq. (18), in principle, is capable of recovering the intrinsic viscosity of the polyelectrolyte solution. In order to obtain the intrinsic viscosity using this equation, however, one needs to perform the viscosity measurements in very dilute solutions because of the nonlinear variations of the reduced viscosity with concentration.

2.6.2.2 Intrinsic Viscosity

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

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

At a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity (η_{sp} / c_p) varies linearly with the polymer concentration (c_p) similar to that for a neutral macromolecular solution, provided there is an excess of low molar mass electrolyte thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation^{2,144}

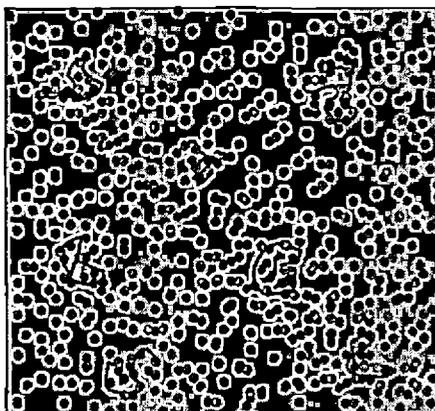


Figure 2.6 Elimination of polyelectrolyte effect by addition of a large excess of a salt

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

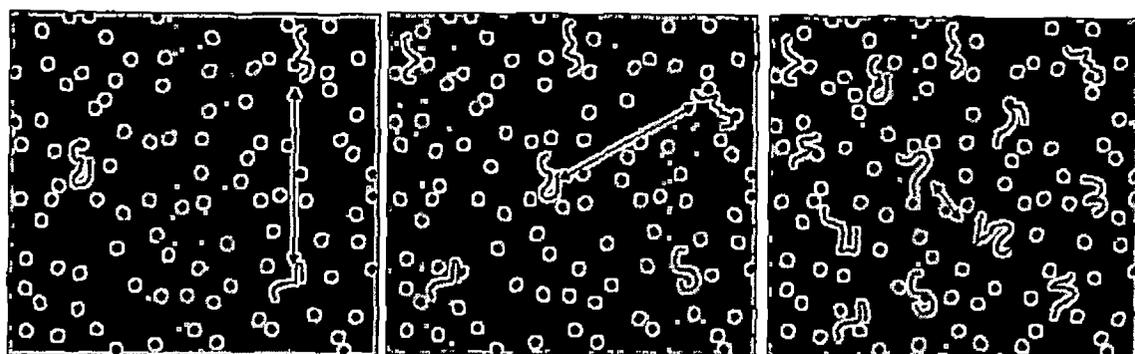
here k_H is the Huggins constant which is a characteristic for a given polymer-solvent system.

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

2.6.2.4 Determination of Intrinsic Viscosity of a Polyelectrolyte by Isoionic Dilution

This is another method for the determination of the intrinsic viscosity of a polyelectrolyte.^{124,145} Following this method, a polyelectrolyte solution in the pure solvent (in absence of any low molar mass salt) is diluted with solutions of increasing concentration of a salt. The dilution of the solution is performed in such a way that after each addition, the total ionic strength of the solution remains the same and equal to that of the original solution due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these conditions the reduced viscosity decreases linearly as one lowers the polyelectrolyte concentration and thus extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength. Moreover, since the ionic environment around the polyions remains unaffected as a result of isoionic dilution, the original conformation of the polyion under salt-free situation is assumed to be preserved.

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



Isoionic Dilution

Figure 2.7 Dilution keeping fixed ionic strength

2.6.3 Partial Molar Volumes of Polyelectrolytes

The apparent molar volume (ϕ_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, ρ the density of the solution and ρ_0 the density of the solvent.

In majority of the polyelectrolyte solutions investigated, the apparent molar volumes were found to remain practically constant over the concentration ranges investigated though it is true that they vary slightly with concentration for a few cases.¹⁴⁷⁻¹⁵² The insensitivity of the ϕ_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 ϕ_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 ϕ_v values.^{153,154}

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

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

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

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

2.7 Present Investigation

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

As pointed out earlier, the main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between ionic

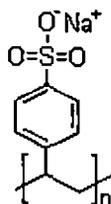


Figure 2.8 Structure of sodium polystyrenesulphonate

Sites in the polymer chain and secondly, the interactions between the polyions and counterions surrounding the polyion chains. The first factor is concerned with expansibility of the polymer chains, whereas the second is not only reflected in counterion binding but also in the amount of solvation and the solvent structure in the vicinity of polyelectrolytes. Both of these factors are related to the relative permittivity of the solvent media. The dissertation aims to address, these aspects of polyelectrolyte solutions with particular reference to the system mentioned above.

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

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

chemical characteristics midway between protic and dipolar aprotic solvents. Simple consideration of molecular structures indicates that due to the presence of electron repelling CH_3CH_2- group, 2-ethoxyethanol is more basic than ethylene glycol and water. Also, the restricted availability of the acidic H atom of OH group makes 2-ethoxyethanol molecules less acidic than ethylene glycol and water, thus imparting a "quasi-*aprotic*" character to it. That is, it behaves as an amphiprotic dipolar solvent with low relative permittivity ($D = 13.38$ at 298.15 K).¹⁶⁵ Moreover, it is completely miscible in water and the relative permittivities of the mixed solvent media could be varied over a wide range. Cellosolves find extensive use as solvents and solubilizing agents in many industries with interests ranging from pharmaceutical to plastic products.^{166,167} Extensive investigations have, so far, been made on 2-ethoxyethanol as well as in its mixtures with water.¹⁶⁸⁻¹⁸⁰ It would be, therefore, interesting to investigate the behaviour of a polyelectrolyte in these mixed solvents.

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Chapter 3

Experimental

3.1 Chemicals

3.1.1 Sodium Polystyrenesulphonate

The anionic polyelectrolyte sodium polystyrenesulphonate with a molecular weight of 70000 and a degree of sulfonation of 1.0 was purchased from Aldrich Chemical Company, Inc., and was purified by dialysis.^{1,2} 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,³ $[\eta] = 1.39 \times 10^{-4} M^{0.72}$, where $[\eta]$ is the intrinsic viscosity, and M is the average molecular weight. The absorption coefficient of the sodium polystyrenesulphonate solutions used at 261 nm, which is considered to be a characteristic indicator of the sample purity,² 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.

3.1.2 Sodium Chloride

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

3.2 Solvents

3.2.1 2-Ethoxyethanol

2-Ethoxyethanol (G.R.E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $1.8277 \text{ mPa}\cdot\text{s}$ at 298.15 K; these values are in good agreement with the literature values.⁴

3.2.2 Water

Triply distilled water was used for the preparation of the experimental solutions. Water was first deionized and then distilled in an all glass distilling apparatus using alkaline KMnO_4 solution. The distilled water was then redistilled twice. Precautions were taken to

prevent contaminations from CO₂ and other impurities. The triply distilled water had a specific conductance of less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 308.15 K.

3.3 Preparation of the Mixed Solvents

2-Ethoxyethanol–water mixed solvents were prepared by mixing requisite amounts of 2-ethoxyethanol and water by mass. The physical properties, namely the densities (ρ_0), the coefficients of viscosities (η_0) and the relative permittivities (D) of these mixed solvents used at 308.15, 313.15, 318.15 and 323.15 K are reported in Table 3.1. The relative permittivities of 2-ethoxyethanol–water mixtures at the experimental temperatures were obtained with the equations as described in the literature⁵ using the literature density and relative permittivity data of the pure solvents^{4,6} and the densities of the mixed solvents given in Table 3.1.

3.4 Methods

3.4.1 Conductance Measurements

Conductance measurements were carried out 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^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers⁷ using aqueous potassium chloride solution. The measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ 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.

3.4.2 Density Measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 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 using their literature values.^{6,8} The precisions of the density measurements were always within $3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. The measurements were performed in a water bath which was maintained within an accuracy of 0.01 K of the desired temperature by means of an electronic relay and a contact thermometer.

3.4.3 Viscosity Measurements

The viscometric measurements were performed at 308.15, 313.15, 318.15 and 323.15 K using a Schultz-Immergut-type viscometer⁹ 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 ± 0.01 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.^{10,11} 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 (η_{sp}/c_p ; η_{sp} = specific viscosity and c_p = polyelectrolyte concentration) is obtained from

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

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

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.

3.5 References

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Table 3.1 Densities (ρ_0), Coefficients of Viscosities (η_0) and Relative Permittivities (D) of 2-Ethoxyethanol–Water Mixtures Containing 10, 25, 40 and 50 Mass % of 2-Ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K

T (K)	ρ_0 (g·cm ⁻³)	η_0 (mPa·s)	D
10 mass % 2-ethoxyethanol			
308.15	0.98926	1.3099	69.87
313.15	0.99287	1.1017	68.13
318.15	0.99019	0.8961	66.55
323.15	0.99536	0.8943	65.08
25 mass % 2-ethoxyethanol			
308.15	0.99758	1.8430	60.13
313.15	0.99245	1.5293	58.70
318.15	0.98807	1.2738	57.37
323.15	0.98394	1.0923	56.11
40 mass % 2-ethoxyethanol			
308.15	0.99747	1.9545	50.54
313.15	0.99101	1.7015	49.28
318.15	0.98696	1.4274	48.14
323.15	0.98378	1.2317	47.10
50 mass % 2-ethoxyethanol			
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96

Chapter 4

The Effects of Concentration, Relative Permittivity, and Temperature on the Transport Properties of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

4.1 Introduction

Polyelectrolytes are polymers having ionizable groups, which in polar solvents, can dissociate into charged polymer chains and small counterions of opposite charge.¹⁻² Solution properties of polyelectrolytes, both in the presence and in the absence of an added salt, differ considerably from those of neutral macromolecular solutions or those of simple electrolytes. The origin of this specificity lies in the combination of properties derived from long-chain molecules with those derived from charge interactions. The high charge density on the macroion produces a strong ionic field which attracts counterions. This strong ionic interaction is the source of the characteristic properties of polyelectrolytes. Current interest in charged polymer solutions, in particular, in high-molecular weight ionic macromolecules, is supported by the needs of biophysics since biopolymers are usually charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behaviour.³ In accounting for the solution behaviour of biological and synthetic polyelectrolytes, elucidation of the interactions between counterions and charged groups on the polyion are of essential importance. Polyelectrolyte effect includes both deviations from the behaviour of neutral polymers caused by the existence of charges along the polymer chain and deviations from the behaviour of the electrolytes caused by the fixation of one sort of charges on the polymer chain. Therefore, in addition to the method of macromolecular characterization, electrochemical techniques have also been applied to investigate the solution behaviour of polyelectrolytes. The specific conductance and the equivalent conductivity, Λ , 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. In spite of various attempts by different investigators, a completely satisfactory theory to provide a priori description of the electrolytic conductivity of polyelectrolyte solutions has not yet been developed.⁴⁻⁶

However, the description of different electrical properties of polyions in aqueous solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory⁷⁻¹⁰ that, under some aspects, can be considered equivalent to the Poisson-Boltzmann cylindrical cell model.¹¹⁻¹⁵ 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 groups 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 continuous medium characterized by a spatially uniform dielectric constant. Interactions among polyions are neglected, the theory being addressed to highly diluted solutions. The basic idea is that if the charge density (ξ) of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy $k_B T$. On the basis of these assumptions, this approach has been successfully applied to different polyelectrolyte systems, and numerous experiments have strongly suggested the validity of this model.¹⁶⁻²²

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by^{7,23,24}

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

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. A limiting law of electrical conductivity for a salt-free polyelectrolyte solution is related to ξ by the following equation.^{8,23,25}

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

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is counterion-polyion interaction parameter given by^{7,23,24}

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

In contrast to Huizenga,²⁶ 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 free counterions rather it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolyte,⁹ and it follows for counterions with a charge of z_c

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

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

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

with η_0 being the coefficient of viscosity of the solvent. In Eq. (5), κ is the Debye screening constant, which is defined by

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

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

As far as we know there is very little work in the literature dealing with the effect of the medium and temperature on the interaction between a polyion and its counterions.^{1,27,28} In this chapter, the results are reported for conductivity measurements on sodium polystyrenesulphonate, an anionic polyelectrolyte, in 2-ethoxyethanol–water mixed solvent media with varying relative permittivity at different temperatures. The aim of the present work is to analyze the influence of concentration, medium and temperature on the extent of polyion-counterion interaction and on the mobility of the polyelectrolyte species. The

experimentally determined equivalent conductivity values have also been compared with those obtained theoretically from the Manning counterion condensation model. The solvent 2-ethoxyethanol has been chosen because it is soluble in water in all proportions and it has a low relative permittivity solvent ($D = 13.38$ at 298.15 K)²⁹ so that the relative permittivity of the mixed solvent media can be varied over a wide range.

4.2 Experimental

2-Ethoxyethanol (G. R. E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497\text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $1.8277\text{ mPa}\cdot\text{s}$ at 298.15 K ; these values are in good agreement with the literature values.²⁹ Triply distilled water with a specific conductance 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 2-ethoxyethanol–water mixed solvents used in this study at 308.15 , 313.15 , 318.15 , and 323.15 K are reported in Table 4.1. The relative permittivity of 2-ethoxyethanol–water mixtures at the experimental temperatures were obtained with the equations as described in the literature³⁰ using the literature density and relative permittivity data of the pure solvents^{29,31} and the densities of the mixed solvents are given in Table 4.1.

Sodium polystyrenesulphonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was *ca.* 70000 and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

Conductance measurements were carried out 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^{-1} and having an uncertainty of 0.01% . The cell was calibrated by the method of Lind and co-workers³² using aqueous potassium chloride solution. 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.^{33,34} Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. The overall reproducibility of the conductance measurements was always found to be within $\pm 0.025\%$. 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, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

4.3 Results and Discussion

4.3.1 Experimental Equivalent Conductivity

The experimental equivalent conductivities for sodium polystyrenesulphonate as a function of the square root of the polymer concentration in four different 2-ethoxyethanol–water mixtures (containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol) at 308.15, 313.15, 318.15 and 323.15 K are shown in Figures 4.1 to 4.4. The equivalent conductivities exhibit, in general, a slight and monotonous increase with decreasing polymer concentration passing through a maximum in some cases within the concentration range investigated here. The experimental error associated with the measurements was found to be within $\pm 0.10\%$ which is always smaller than the concentration variation of the measured equivalent conductivities.

The effects of temperature and relative permittivity on the equivalent conductivity values are also evident from these figures. At each mass percent of 2-ethoxyethanol in 2-ethoxyethanol–water mixture, the Λ values are found to increase with increasing temperature over the entire concentration range investigated. This is quite expected because as the relative permittivity of the medium increases, interaction between polyion and counterions decreases which results in a higher mobility of the conducting species and hence the polyelectrolyte as a whole. Increasing temperature, on the other hand, is expected to increase the mobility as manifested in these figures.

4.3.2 Comparison with Manning Counterion Condensation Theory

Now we will compare the experimental values of equivalent conductivity with those calculated using the Manning counterion condensation theory, Eqs. (2) to (4). In order to calculate the theoretical equivalent conductivities, the required values for the limiting equivalent conductivity of the counterion, λ_c^0 in 10, 25, 40 and 50 mass percent of 2-ethoxyethanol mixtures were also measured and are given in Table 4.1. The charge density parameters, ξ , were calculated using a segment length²¹ of 2.52 \AA having one charged group and these are included in Table 4.2. The theoretical values of λ_p and hence of Λ , are dependent on a , the radius of the polyion cylinder. Obviously, the assignment of a cylindrical radius to any polymer chain can only be a rough approximation at best, but fortunately λ_p is not strongly dependent on a , and change in concentration dependence of λ_p upon varying a between realistic values is small. A cylindrical radius of 8 \AA was used for the present analysis.²¹

A graphical representation of the experimental values (points) along with the theoretical predictions (solid lines) is given in Figure 4.5 at a selected temperature in 2-ethoxyethanol–water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated using the charge density parameter, ξ , obtained from the molecular structure of the polyelectrolyte, (*cf.* Figure 4.5). The same situation of positive deviation^{35,36} as well as negative deviation^{20,28} from the experimental values was also noticed for other polyelectrolyte solutions. The discrepancy between the experimental and predicted Λ values for sodium polystyrenesulphonate in all 2-ethoxyethanol–water mixtures and at all temperatures investigated is very similar. Lower calculated equivalent conductivities are, therefore, a consequence of Manning theory which predicts too small values for the fraction of uncondensed counterions.

It is interesting to note that the equivalent conductivity calculated here is found to be highly sensitive towards ξ and a semiquantitative description of the experimental data is obtained only if the charge density parameter ξ is decreased from its structural value. The dashed lines in Figure 4.5 display the respective calculation using the optimum values of ξ which provide significant improvement over the Manning results although quantitative fits were not achieved. The charge density parameters, ξ , which describe the experimental results best along with the respective standard deviation of fits are given in Table 4.2. In the case of this flexible polyelectrolyte, this could be rationalized by assuming an “effective charge density parameter” which is lower than the value obtained from the structural data and adjusted to match the experimental data. The reason for a lower effective ξ was sought in the high charge density along the flexible polyion chain due to the higher dissociation of polyion than that predicated by the Manning theory. Hence the overall conductance value is increased. Other possible reasons for the observed differences between the experiment and theory include deviation from the rodlike model due to possible kinking in the structure of the polyelectrolyte, possible polyion-polyion interaction, interaction between the uncondensed counterions and specific interaction between polyion and the counterions.^{11,24,37-39} Another possible reason may be sought in a locally varying relative permittivity. The immediate neighbourhood of the macroion may exhibit a considerably higher relative permittivity than the bulk.⁴⁰ This must necessarily lead to a weaker interaction of the macroion with the counterions as observed in the present investigation. A further possibility is that the Manning theory, based on the assumption of an infinitely long polymer chain model, might be

inadequate for treating condensation phenomena, since in the limit of dilution, it was found that counterion condensation does not occur for polyion of finite length. Finally, it may be pointed out that even the “effective charge density parameter” does not quantitatively reproduce the experimental results indicating that there might be concentration dependent change in the parameter which has not been taken into account in the Manning theory.

4.3.3 Influences of Relative Permittivity and Temperature

The effects of relative permittivity and temperature on the equivalent conductivity values are directly evident from Figures 4.1 to 4.4. At each temperature, the λ values are found to decrease with decreasing relative permittivity in going from 10 to 50 mass percent 2-ethoxyethanol–water mixtures over the entire concentration range investigated. An increase in temperature, on the other hand, is found to increase the polyelectrolyte solution conductivity in a given solvent medium as manifested in these figures.

At a given temperature, f values are found to decrease as the solvent medium gets richer in 2-ethoxyethanol (Figure 4.6). With the increase in the 2-ethoxyethanol content, the relative permittivity of the medium decreases at a given temperature. Lower relative permittivity promotes greater counterion-binding and hence results in a lower amount of uncondensed counterions in going from 10 to 50 mass percent of 2-ethoxyethanol in the mixed solvent media over the entire range of temperatures investigated.

4.4 Conclusions

Experimental results for the equivalent conductivity of salt-free solutions of an anionic polyelectrolyte, sodium polystyrenesulphonate, in 2-ethoxyethanol–water mixed solvent media have 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 investigated in a given mixed solvent medium whereas these values 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 cannot be quantitatively described by this theory. Lower calculated equivalent conductivities are a consequence of Manning theory which predicts too small values for the fraction of uncondensed counterions. A semiquantitative description of the experimental data is, however, obtained if the charge density parameter is adjusted to a value lower than the structural value. The deviations indicate higher dissociation of the polyion than that predicted

by the theory, and / or a higher relative permittivity in the vicinity of the polyion chain. Other possible reasons for the observed deviation from the Manning theory have also been discussed. Counterion-binding onto the polyion chain is found to increase as the medium gets richer in 2-ethoxyethanol. The increase in the temperature, in general, has been shown to increase the fraction of uncondensed counterions in each of the mixed solvent medium investigated with minor exception in 10 mass percent 2-ethoxyethanol-water mixture. Finally, it should be pointed out that the Manning law applies only at exceedingly low concentrations which cannot be attained by experiments. Hence, the quantitative conclusion drawn from this law cannot be compared to experimental data in a quantitative manner. This might, however, provide a qualitative guideline.

4.5 References

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Table 4.1 Densities (ρ_0), coefficient of viscosities (η_0) and relative permittivities (D) of 2-Ethoxyethanol–Water Mixtures Containing 10, 25, 40 and 50 Mass Percent of 2-Ethoxyethanol at 308.15, 313.15, 318.15, and 323.15 K and the Corresponding λ_c^0 Values of the Sodium Ion

T (K)	ρ_0 ($\text{g} \cdot \text{cm}^{-3}$)	η_0 ($\text{mPa} \cdot \text{s}$)	D	λ_c^0 ($\text{S} \cdot \text{cm}^2 \cdot \text{Eqv}^{-1}$)
10 mass % 2-ethoxyethanol				
308.15	0.98926	1.3099	69.87	46.63
313.15	0.99287	1.1017	68.13	50.33
318.15	0.99019	0.8961	66.55	52.17
323.15	0.99536	0.8943	65.08	55.47
25 mass % 2-ethoxyethanol				
308.15	0.99758	1.8430	60.13	37.42
313.15	0.99245	1.5293	58.70	40.13
318.15	0.98807	1.2738	57.37	42.87
323.15	0.98394	1.0923	56.11	45.80
40 mass % 2-ethoxyethanol				
308.15	0.99747	1.9545	50.54	29.82
313.15	0.99101	1.7015	49.28	32.04
318.15	0.98696	1.4274	48.14	35.30
323.15	0.98378	1.2317	47.10	38.16
50 mass % 2-ethoxyethanol				
308.15	0.99361	1.9234	44.30	25.61
313.15	0.98514	1.7195	43.03	27.81
318.15	0.98004	1.4552	41.95	31.30
323.15	0.97610	1.2762	40.96	34.26

Table 4.2 Calculated, from Eq. (1), and Best Fitted Charge Density Parameter, ξ , in 2-Ethoxyethanol–Water Mixtures at Temperatures 308.15, 313.15, 318.15, and 323.15 K

Mass % of cosolvent	ξ value							
	T = 308.15 K		T = 313.15 K		T = 318.15 K		T = 323.15 K	
	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)
10	3.08 (37.43)	1.08 (2.00)	3.11 (40.03)	1.14 (2.73)	3.13 (44.39)	1.12 (3.09)	3.15 (50.78)	1.03 (2.86)
25	3.58 (26.10)	1.19 (1.50)	3.61 (28.11)	1.21 (1.68)	3.63 (33.15)	1.15 (1.63)	3.66 (36.24)	1.15 (1.77)
40	4.26 (16.90)	1.48 (1.33)	4.30 (18.15)	1.50 (0.77)	4.33 (22.06)	1.42 (0.72)	4.36 (23.58)	1.44 (1.27)
50	4.86 (12.14)	1.74 (0.62)	4.92 (14.65)	1.64 (0.17)	4.97 (15.28)	1.74 (1.37)	5.01 (19.41)	1.58 (1.33)

^a Obtained assuming fully stretched polyion.^b Standard deviation of fit.

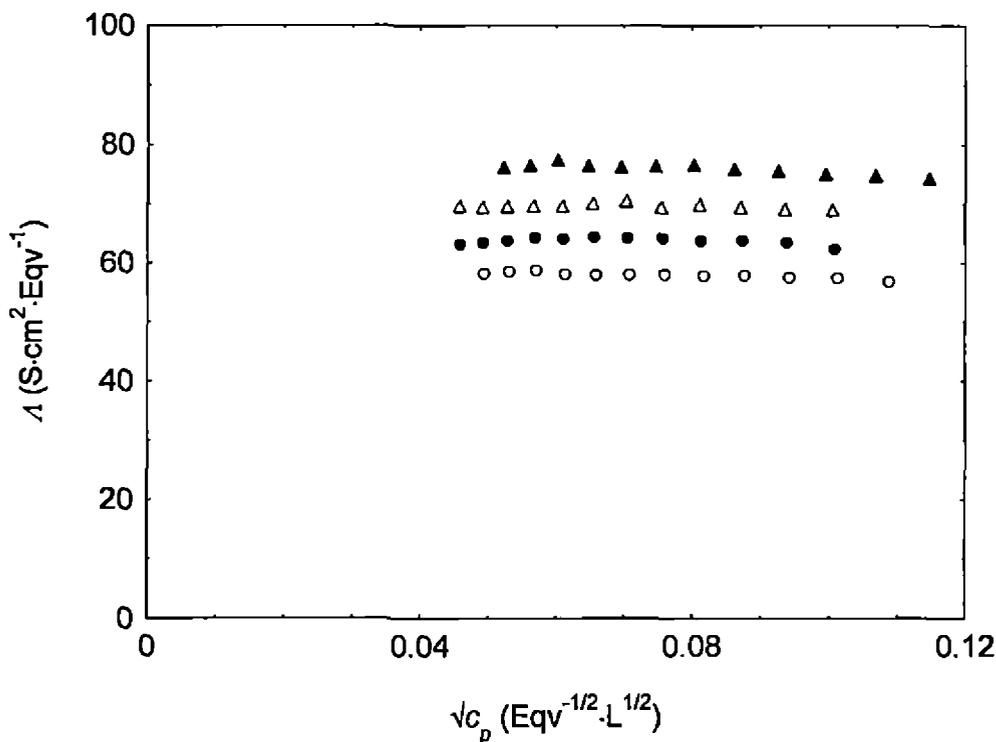


Figure 4.1 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 10 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

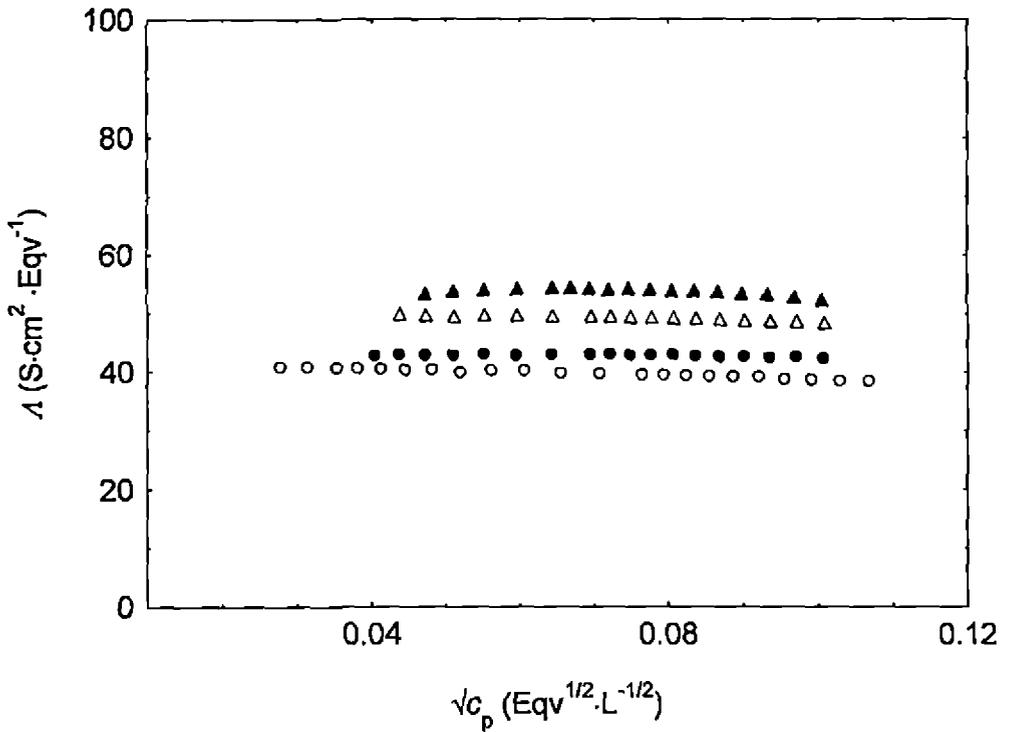


Figure 4.2 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

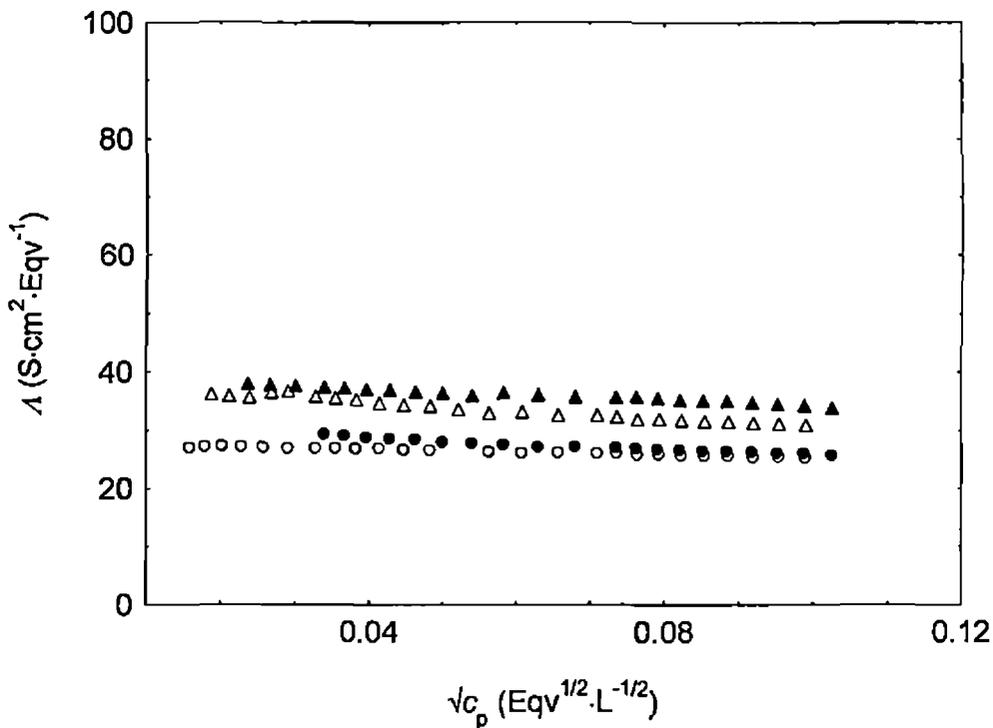


Figure 4.3 Equivalent conductivities (λ) of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

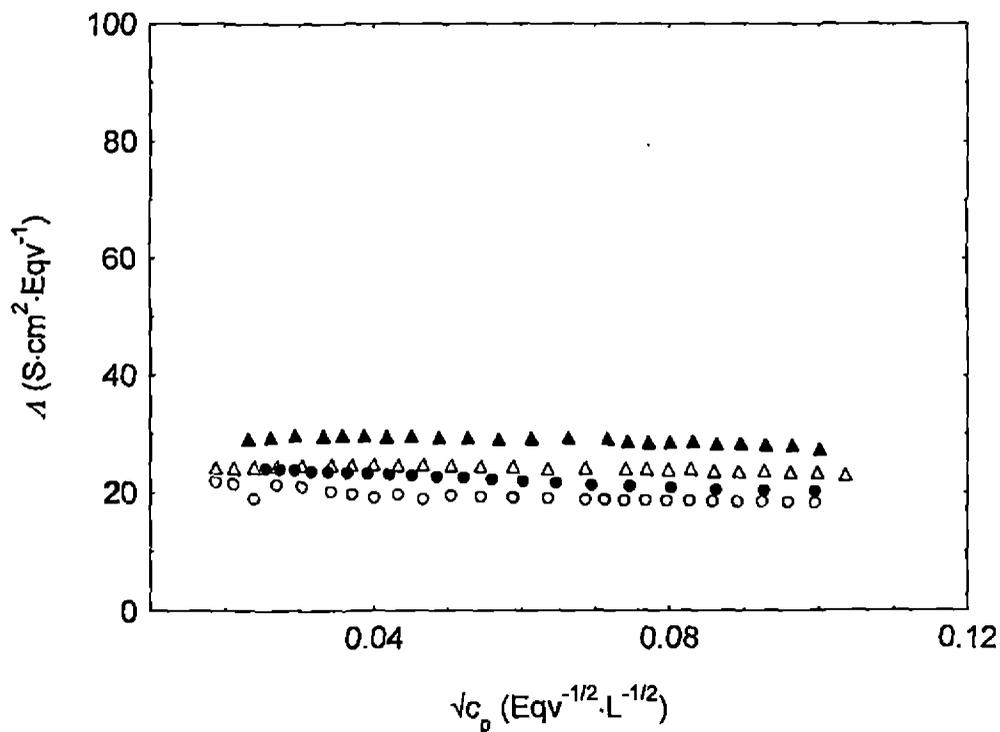


Figure 4.4 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 50 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

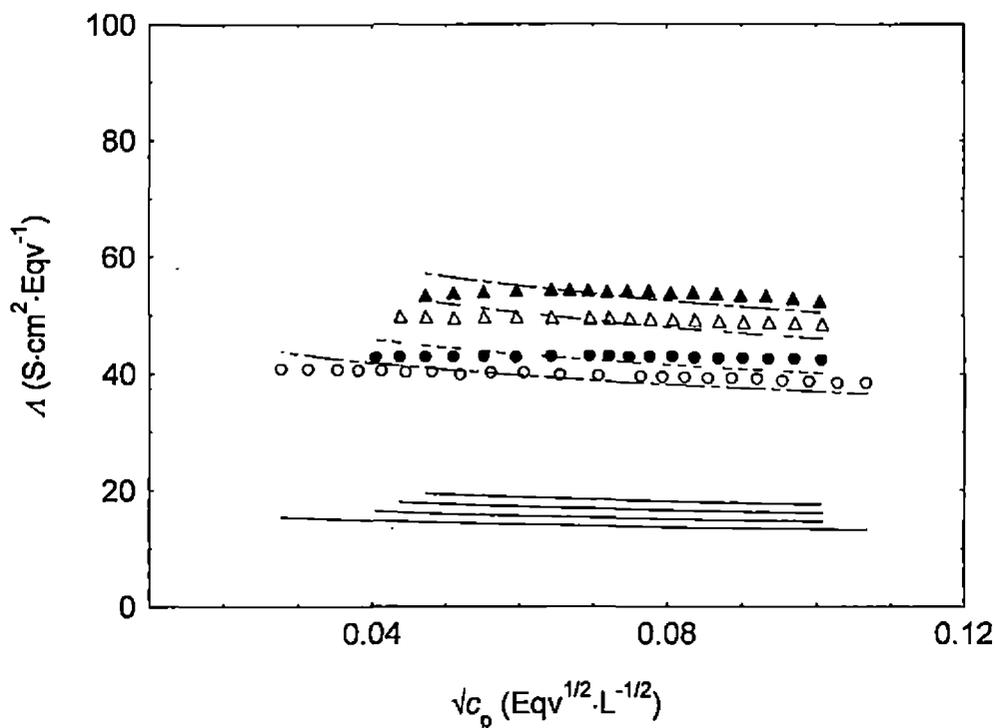


Figure 4.5 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixture as a function of square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles) along with those predicted by the Manning counterion condensation theory (continuous lines) and those obtained using the effective charge density parameter (broken lines) as described in the text.

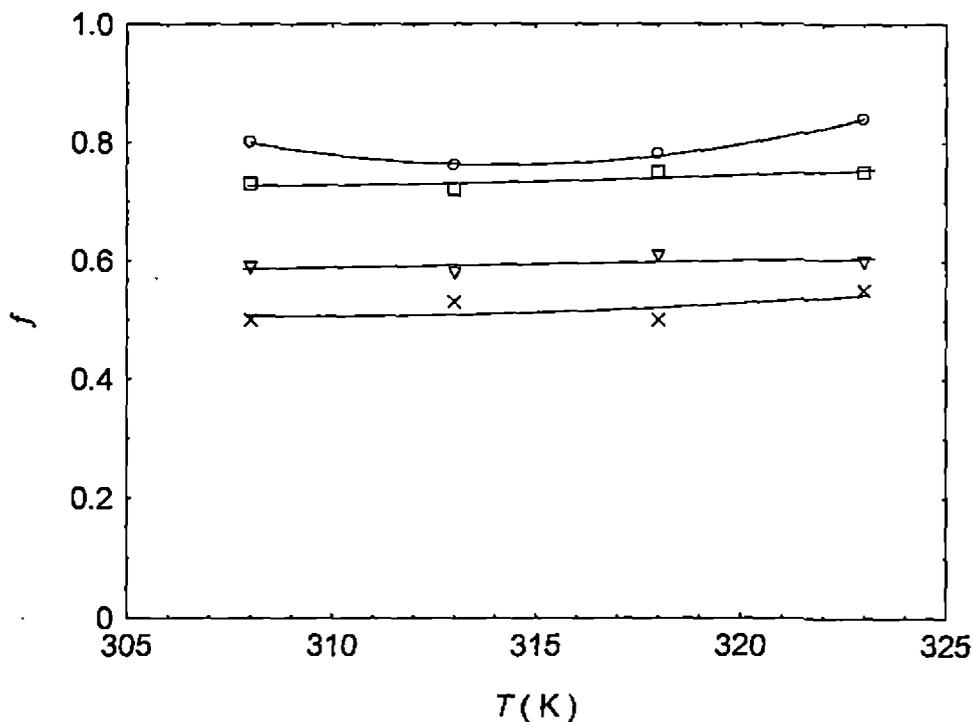


Figure 4.6 Fractions of uncondensed counterions of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixtures as a function of the temperatures in 10 (open circle), 25 (square), 40 (triangle) and 50 (cross) mass percent of 2-ethoxyethanol.

Chapter 5

Conductance of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media: An Analysis using the Scaling Theory Approach

5.1 Introduction

In Chapter 4 it has been observed that the Manning counterion condensation model could not explain the conductivity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media. The disagreement indicates that this theory provides comparatively small values for the fraction of uncondensed counterions for this system. Possible reasons for the observed disagreement have also been analyzed. However, very significant conclusions regarding the structures of the polyion and its counterions are achieved through an analysis of the results.

Later Colby *et al.*¹ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*² put forward an equation (with one adjustable parameter) to describe the conductivity of a semidilute polyelectrolyte solution. It would be of interest to apply this model for the analysis of the conductivity data which are in the semidilute concentration region since the application of the Manning model to these systems is, however, less straightforward because these semidilute macroions do not assume a fully stretched conformation in solution.

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

Under the condition of $g/g_e = \xi_0/\xi_e$ and making use of the fact that the electrostatic blobs are space filling ($g = c_p \xi_0^3$, c_p being the number density of monomers), the specific conductivity of a polyelectrolyte in a semidilute solution in absence of an added salt is, within this model, given by

$$\kappa = f c_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (1)$$

where λ_c^0 is the limiting equivalent conductivity of the counterions and η_0 is the coefficient of viscosity of medium.

The above expression given by Colby *et al.*¹ is derived taking into account the scaling arguments proposed by Dobrynin *et al.*² 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 (adjustable) parameter f , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory.

This new model for semidilute polyelectrolyte conductivity has been applied, so far, to a limited number of aqueous polyelectrolytes^{1,3,4} and good agreement with the experiment was observed. 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 polystyrenesulphonate in acetonitrile–water mixed solvent media.⁵

5.2 Results and Discussion

Graphical representation of the experimental equivalent conductance (Λ) values (points), and the Manning predictions (continuous lines) are shown in Figure 4.5 (Chapter 4) at 308.15, 313.15, 318.15 and 323.15 K in 2-ethoxyethanol–water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. Possible reasons for the deviation and their implication for the elucidation of the structure of the polyelectrolyte solutions have been adequately discussed in the previous chapter. The deviation probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies the Manning counterion condensation model. By

estimating the overlap concentration (c^*) for the polymer chain investigated using the following equation,⁶ one can understand the reason for the failure of the Manning model.

$$c^* = \frac{1}{N_A L^2 a} \quad (2)$$

where N_A is the Avogadro's Number, L the contour length and a the monomer length. It is observed that the polymer solutions used in the present study are mostly in the semidilute regime ($c_p > c^* \approx 1 \times 10^{-3} \text{ Eqv} \cdot \text{L}^{-1}$) where the Manning limiting law does not apply.

For semidilute polyelectrolyte solutions we, therefore, have made an effort to analyse the present conductivity data using the scaling theory approach as proposed by Colby *et al.*¹ for semidilute polyelectrolyte solutions.

Since the present 2-ethoxyethanol–water mixtures are poor-solvents for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule and hence we use a value of 5 \AA^0 as the effective monomer size (b) as suggested by Colby *et al.*¹ while analyzing the data on the basis of the Colby model.

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) under poor solvent condition are given by¹

$$\xi_e = b \left(\frac{f}{f^2} \right)^{-1/3} \quad (3)$$

and

$$\xi_0 = (cb)^{-1/2} \left(\frac{f}{f^2} \right)^{-1/3} \quad (4)$$

Therefore, an estimate of polyelectrolyte equivalent conductivity in the semidilute regime is provided by Eq. (1) in conjunction with Eq. (3) and Eq. (4).

In Figures 5.1 to 5.5, the predictions of the Colby model (dashed lines) for the semidilute regime have been compared with the experimental data. The dashed lines in Figures 5.1 to 5.5 display the results of the calculation using the optimum values of f . The fractions of uncondensed counterion (f) which describe the experimental results best along with the respective standard deviations of fits are given in Table 5.1. Figures 5.1 to 5.5 reveal an excellent agreement of the experimental results with those predicted by the scaling theory approach using only one adjustable parameter f .

5.3 Conclusions

We have, thus, been able to quantitatively describe the electrical conductivity data of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions. The values of f listed in Table 5.1 indicate a lower level of counterion condensation as compared to the Manning model.

5.4 References

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Table 5.1 Fraction of Uncondensed Counterions (f) and the Standard Deviations(σ) of Fit for Sodium Polystyrenesulphonate in the Absence of an Added Salt at 308.15, 313.15, 318.15 and 323.15 K in 2-Ethoxyethanol–Water mixed Solvent Media as Obtained According to Eq. (1)

T (K)	Mass % of Cosolvent	f	$\sigma \times 10^6$
308.15	10	0.45	3.78
	25	0.41	4.20
	40	0.26	7.78
	50	0.25	5.35
313.15	10	0.43	3.44
	25	0.41	7.66
	40	0.25	3.48
	50	0.24	3.97
318.15	10	0.40	3.37
	25	0.39	5.65
	40	0.26	5.15
	50	0.24	5.04
323.15	10	0.38	3.36
	25	0.35	5.67
	40	0.24	3.86
	50	0.23	4.45

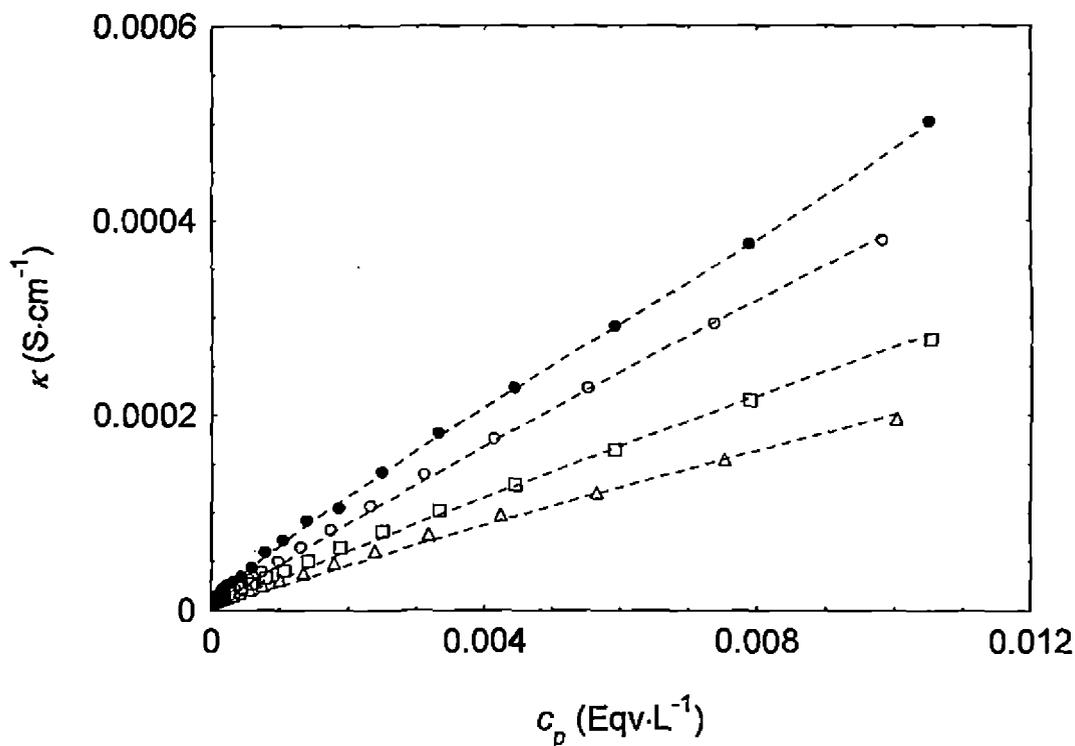


Figure 5.1 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 308.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (Δ) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

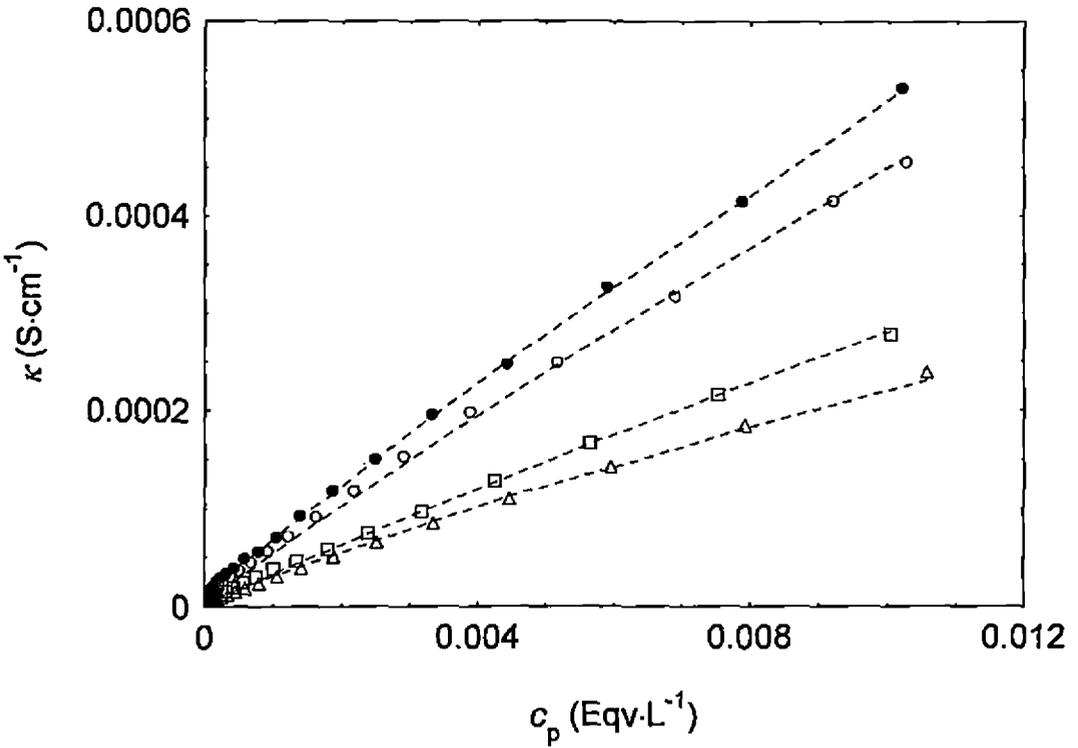


Figure 5.2 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 313.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (Δ) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

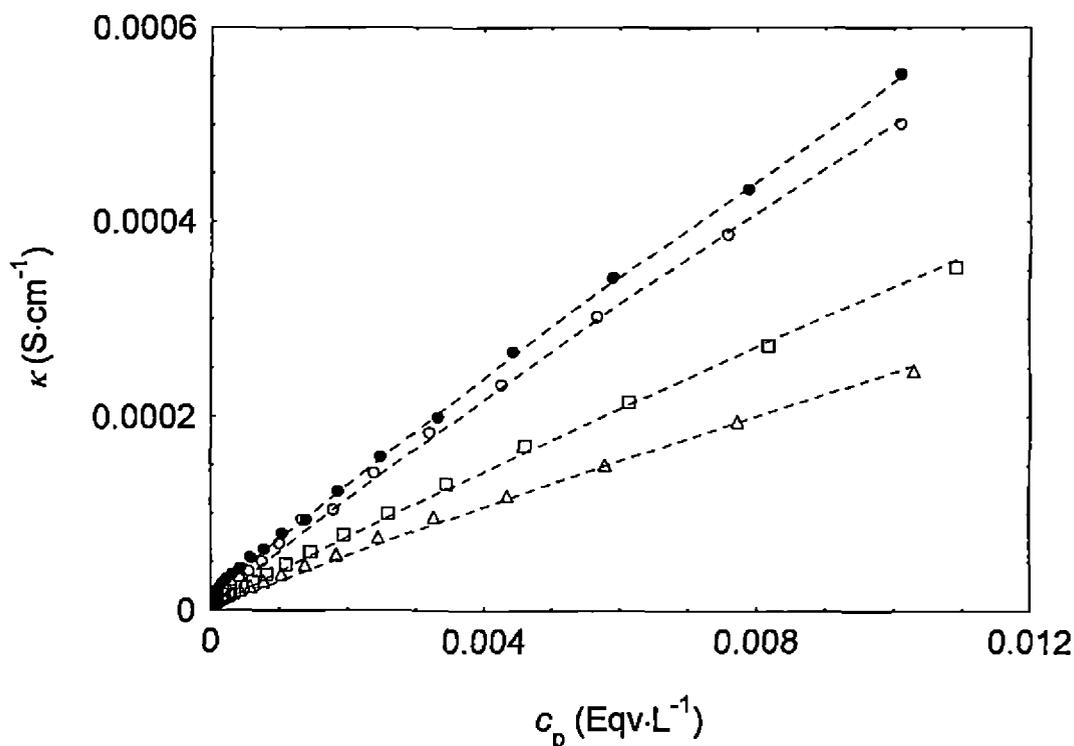


Figure 5.3 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 318.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (Δ) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

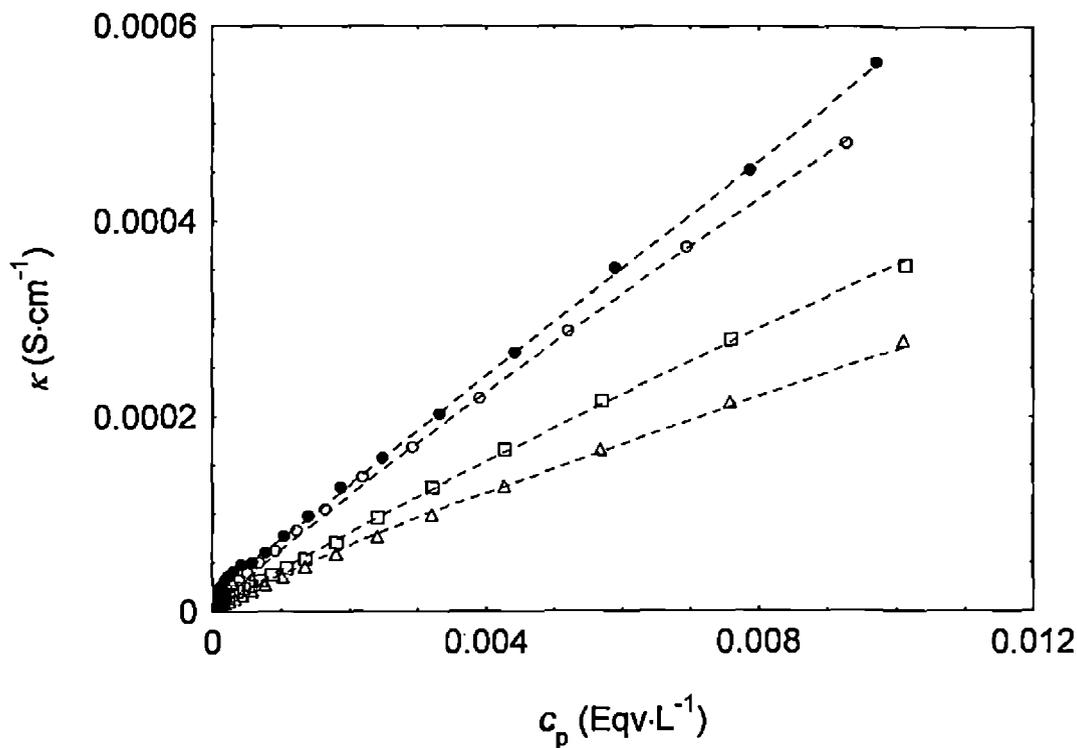


Figure 5.4 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 323.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (Δ) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

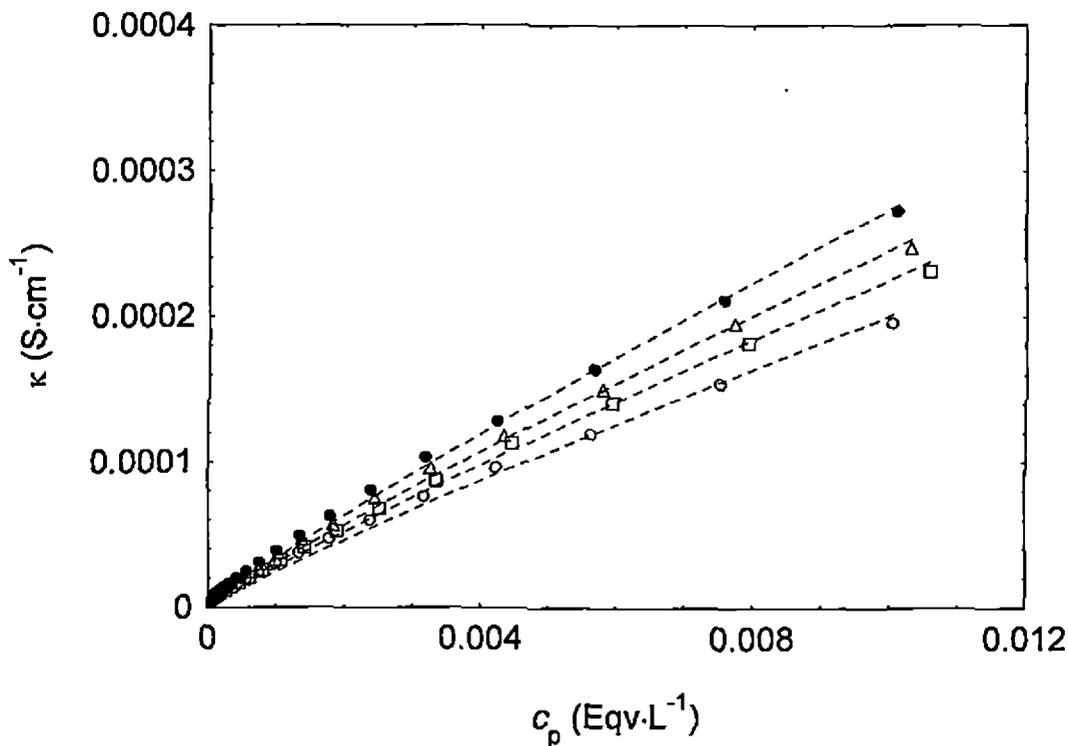


Figure 5.5 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at temperatures of 308.15(○), 313.15(□), 318.15(△) and 323.15 K (●) in 2-ethoxyethanol–water mixtures with 50 mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

Chapter 6

Electrical Conductances of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media in the Presence of Sodium Chloride at 308.15, 313.15, 318.15 and 323.15 K

6.1 Introduction

We have reported the results of conductivity measurements on salt-free solutions of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures in Chapter 4. The addition of salts to a polyelectrolyte solution might change its conductivity behaviour considerably, and hence studies on the conductivity of polyelectrolytes in the presence of a salt might help elucidate polyion-counterion interactions in polyelectrolyte solutions with added salts.

Although the polyelectrolyte conductivities have been well understood in salt-free solutions¹ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*,² the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning³ first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory⁴ without much success. In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the “primitive additivity”) of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.⁵⁻⁹

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

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

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

However, earlier investigations⁵⁻⁹ suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, Eq. (1).

Ander *et al.*^{5,6} modified the ‘primitive’ additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa = \kappa_p + \kappa_s (D_2 / D_2^0) \quad (2)$$

where D_2 and D_2^0 are the coion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2 / D_2^0 has been used as a quantitative measure⁴ of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s (D_2 / D_2^0)$.

Although the “modified” additivity has been shown to be somewhat better than the “primitive” one, departures from the experimental results are still prominent.⁵⁻⁹ Later Bordi *et al.*¹⁰ evaluated equivalent conductances for a hydrophilic polyion in presence of a salt in the light of the scaling approach² and compared with the experimental values. The agreement is rather good although a quantitative description is still awaiting.

In this chapter, a simple model is introduced to analyze the conductivity of polyelectrolyte in the presence of an added electrolyte based on scaling theory for the conductivity of polyelectrolyte solutions.¹ This model has been extensively tested with data on sodium polystyrenesulphonate in the presence of sodium chloride in 2-ethoxyethanol–water mixed solvent media at different temperatures. The data set used here considers a number of parameters *e.g.*, relative permittivity of the medium, temperature and concentration of the added salt. Moreover, three decades of concentration of the polyelectrolyte were covered. Very good quantitative agreement with only one adjustable parameter has been observed.

6.2 Theory

Here we introduce a simple equation for describing the conductivity behaviour of polyelectrolyte in salt solutions following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*¹ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*²

In semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bears an

electric charge $q_\xi = zefg$ (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 $Q_p = N_\xi q_\xi = zefgN_\xi$, where f is the fraction of uncondensed counterions. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e . This means that for length scales less than ξ_0 , the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0 , the electrostatic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Following Colby *et al.*,¹ the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

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

where c_p is the number density of monomers, λ_c^0 the limiting equivalent conductivity of the counterions and η_0 the coefficient of the viscosity of the medium.

The interactions between the polyion and the counterions will be modified in the presence of an electrolyte and this will result in a different level of counterion condensation, *i.e.*, in a different value of f (designated as f'). The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt can be expressed as

$$\kappa_{p(\text{eff})} = f' c_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (4)$$

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

$$\kappa = \kappa_s + f' c_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (5)$$

This equation, Eq. (5), has one adjustable parameter f' and this could be obtained by the method of a least squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in presence of a salt to Eq. (5) using the measured specific conductance (κ_s) of the salt in the absence of the polyelectrolyte. This value of f' takes care of the changed polyion-counterion interactions under the influence of the added salt. The second term in Eq. (5) is the actual contribution of the polyelectrolyte species towards the total specific conductivity in the presence of an added salt.

6.3 Experimental

2-Ethoxyethanol (G. R. E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g} \cdot \text{cm}^{-3}$ and a co-efficient of viscosity of $1.8277 \text{ mPa} \cdot \text{s}$ at 298.15 K ; these values are in good agreement with literature values.¹¹ Triply distilled water with a specific conductance of $\text{ca. } 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The relative permittivities of 2-ethoxyethanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature¹² using the literature density and relative permittivity data of the pure solvents^{11,13} and the densities of the mixed solvents are given in Table 4.1(Chapter 4).

The sodium salt of polystyrenesulphonic acid employed in these investigations was purchased from the Aldrich Chemical Company. The average molecular weight of the sample was $\text{ca. } 70000$ and a degree of sulphonation of 1.0 and it was purified by dialysis.^{14,15} 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,¹⁶ $[\eta] = 1.39 \times 10^{-4} M^{0.72}$, where $[\eta]$ is the intrinsic viscosity, and M is the average molecular weight. The absorption coefficient of the sodium polystyrenesulfonate solutions used at 261 nm , which is considered to be a characteristic indicator of the sample purity,¹⁵ is found to be $400 \text{ dm}^3 \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$. Spectroscopic examination of the polyelectrolyte sample using this criterion was employed periodically to substantiate the sample purity. Sodium chloride (Fluka) was of puriss grade. This was dried *in vacuo* for a prolonged period immediately before 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 with a cell constant of 1.15 cm^{-1} and

having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers¹⁷ using aqueous potassium chloride solution. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. The details of the experimental procedure have been described earlier.^{18,19} Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results.

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. The experimental uncertainties in density, viscosity, and conductivity were always within 0.02 %, 0.80 %, and 0.03 %, respectively.

6.4 Results and Discussion

The experimental values of specific conductivities (κ) of sodium polystyrenesulphonate in the presence of varying concentrations sodium chloride in 2-ethoxyethanol–water mixtures have been listed as a function of the equivalent polyelectrolyte concentration (c_p) at 308.15, 313.15, 318.15 and 323.15 K in Table 5.1. The specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration at given temperatures and solvent compositions in 2-ethoxyethanol–water mixtures with varying amounts of added NaCl are shown in the Figures 6.1 to 6.12. Figures 6.13 and 6.14, on the other hand, demonstrate the influence of temperature on the specific conductivity versus the polymer concentration profiles. From these figures and also from Table 6.1, it is apparent that for all the solutions studied the specific conductivities increase with polyelectrolyte concentration. Addition of salt increases the specific conductances of the polyelectrolyte-salt solutions as expected. The specific conductances of the polyelectrolyte-salt systems are, in general, found to decrease with increasing amount of 2-ethoxyethanol in the mixed solvent media (shown in the representative Figure 6.15).

Since the present 2-ethoxyethanol–water mixtures are poor solvents for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule, we use a value of 5 \AA^0 as the effective monomer size (b) as suggested by Colby *et al.*¹

Under poor solvent conditions, the electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) are given by¹

$$\xi_e = b(f^{-2}\xi)^{-1/3} \quad (6)$$

$$\xi_0 = (cb)^{-1/2} (f^{-2}\xi)^{-1/3} \quad (7)$$

The specific conductivity values of the polyelectrolyte-salt system as a function of polyelectrolyte concentration in a given solvent medium at a given temperature and for a given salt concentration were fitted to Eq. (5) by the method of least-squares analysis. The best-fitted f' values along with the standard deviations are reported in Table 6.1. In the Figures 6.1 to 6.12 we compare the calculated specific conductivities using the f' values obtained in the semidilute regime (reported in Table 6.1) with those obtained experimentally. From the standard deviations recorded in Table 6.1, as well as from an inspection of these figures, it is directly evident that the present method of analysis reproduced the experimental results even in dilute solutions quite satisfactorily. It should be noted that this vigorous test of the proposed model has been performed with 36 sets of data considering the effect of medium, temperature and concentration of the added simple salt. We have, thus, been able to develop a simple model in describing the specific conductivity behaviour of polyelectrolyte-solutions with added salt.

6.5 Conclusions

The electrical conductances of the solutions of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media containing 25, 40 and 50 mass percent of 2-ethoxyethanol have been reported at 308.15, 313.15, 318.15 and 323.15 K in the presence of sodium chloride. The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter developed in the present study following the model for the electrical conductivity of solutions of semidilute polyelectrolytes without salt proposed by Colby *et al.*¹ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*² Excellent agreement between the experimental results and those obtained using Eq. (5) has always been observed. We expect that the model proposed here provides a universal description of the specific conductivities of polyelectrolyte solutions in the presence of an added electrolyte.

6.6 References

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Table 6.1 Fraction of Uncondensed Counterions (f') and the Standard Deviations (σ) of Fit for Sodium Polystyrenesulphonate in the Presence of NaCl at Temperatures (308.15, 313.15, 318.15 and 323.15) K in 2-Ethoxyethanol–Water Mixed Solvent Media as Obtained According to Eq. (5)

T (K)	Mass % of Cosolvent	c_{NaCl} (mol·L ⁻¹)	f'	$\sigma \times 10^6$
308.15	25	1×10^{-4}	0.40	3.09
		1×10^{-3}	0.38	4.59
		1×10^{-2}	0.34	10.06
	40	1×10^{-4}	0.25	1.14
		1×10^{-3}	0.23	1.82
		1×10^{-2}	0.21	2.37
	50	1×10^{-4}	0.25	0.74
		1×10^{-3}	0.24	1.52
		1×10^{-2}	0.21	2.91
313.15	25	1×10^{-4}	0.40	5.19
		1×10^{-3}	0.35	6.29
		1×10^{-2}	0.33	6.82
	40	1×10^{-4}	0.23	3.40
		1×10^{-3}	0.21	4.01
		1×10^{-2}	0.18	3.77
	50	1×10^{-4}	0.25	1.13
		1×10^{-3}	0.23	1.65
		1×10^{-2}	0.18	5.60
318.15	25	1×10^{-4}	0.38	3.84
		1×10^{-3}	0.35	4.26
		1×10^{-2}	0.32	5.67
	40	1×10^{-4}	0.25	2.45
		1×10^{-3}	0.22	3.62
		1×10^{-2}	0.17	8.48
	50	1×10^{-4}	0.23	1.69
		1×10^{-3}	0.21	2.76
		1×10^{-2}	0.18	5.08
323.15	25	1×10^{-4}	0.34	6.33
		1×10^{-3}	0.31	7.65

Table 6.1 (Continued)

T (K)	Mass % of Cosolvent	c_{NaCl} (mol·L ⁻¹)	f'	$\sigma \times 10^6$
	40	1×10^{-2}	0.28	7.57
		1×10^{-4}	0.24	4.87
		1×10^{-3}	0.22	5.61
	50	1×10^{-2}	0.20	7.69
		1×10^{-4}	0.23	2.32
		1×10^{-3}	0.22	3.90
		1×10^{-2}	0.19	5.10

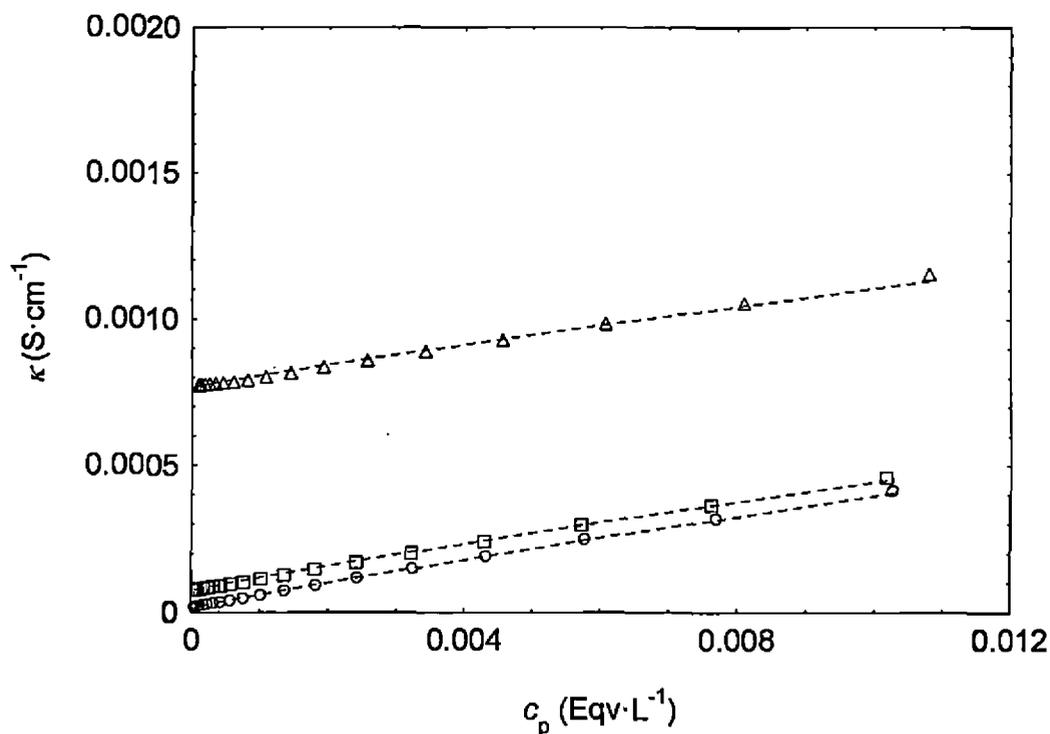


Figure 6.1 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 308.15 K in a 2-ethoxyethanol–water mixture with 25 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

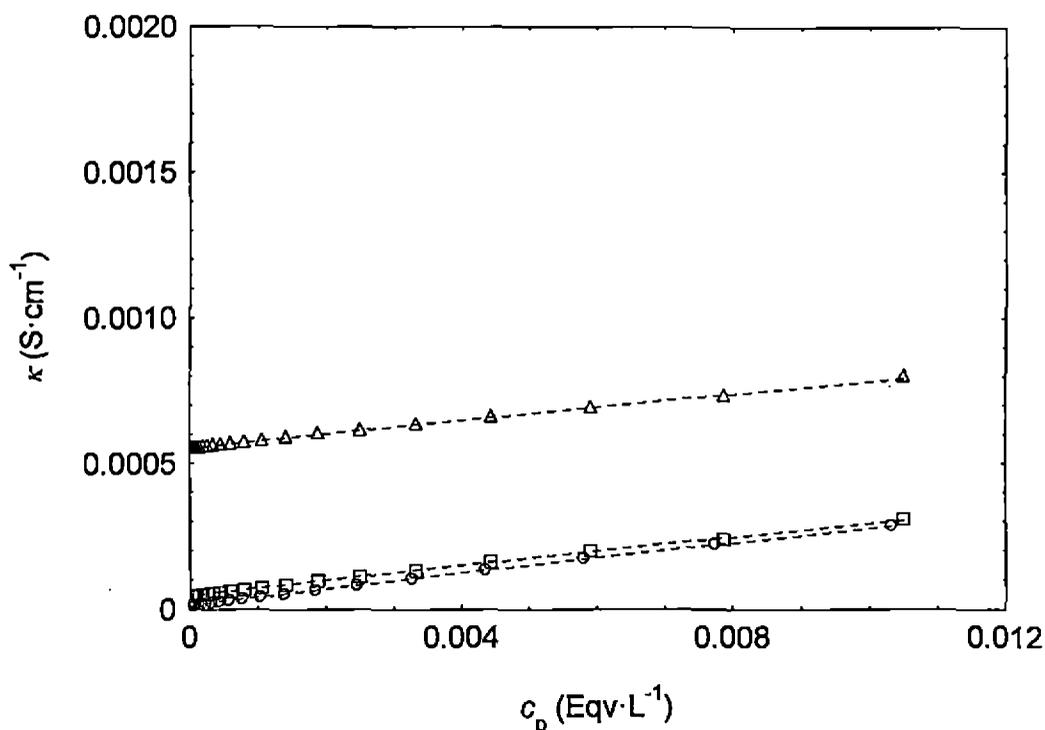


Figure 6.2 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 308.15 K in a 2-ethoxyethanol–water mixture with 40 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) mol·L⁻¹ NaCl respectively (see text).

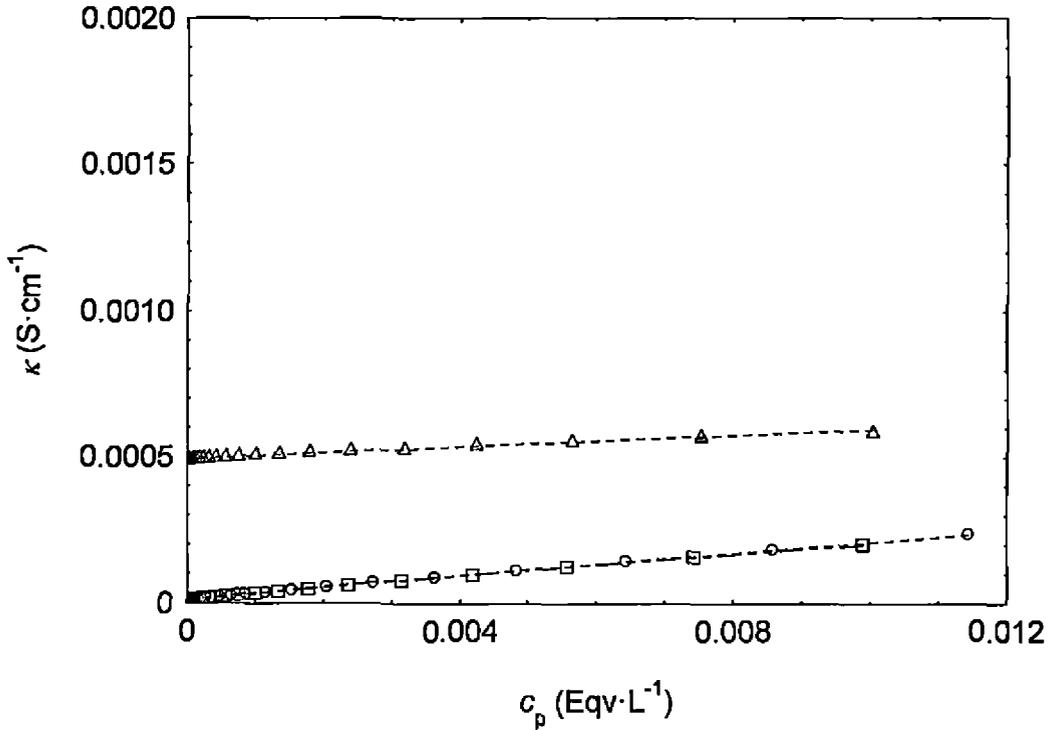


Figure 6.3 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 308.15 K in a 2-ethoxyethanol–water mixture with 50 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) mol·L⁻¹ NaCl respectively (see text).

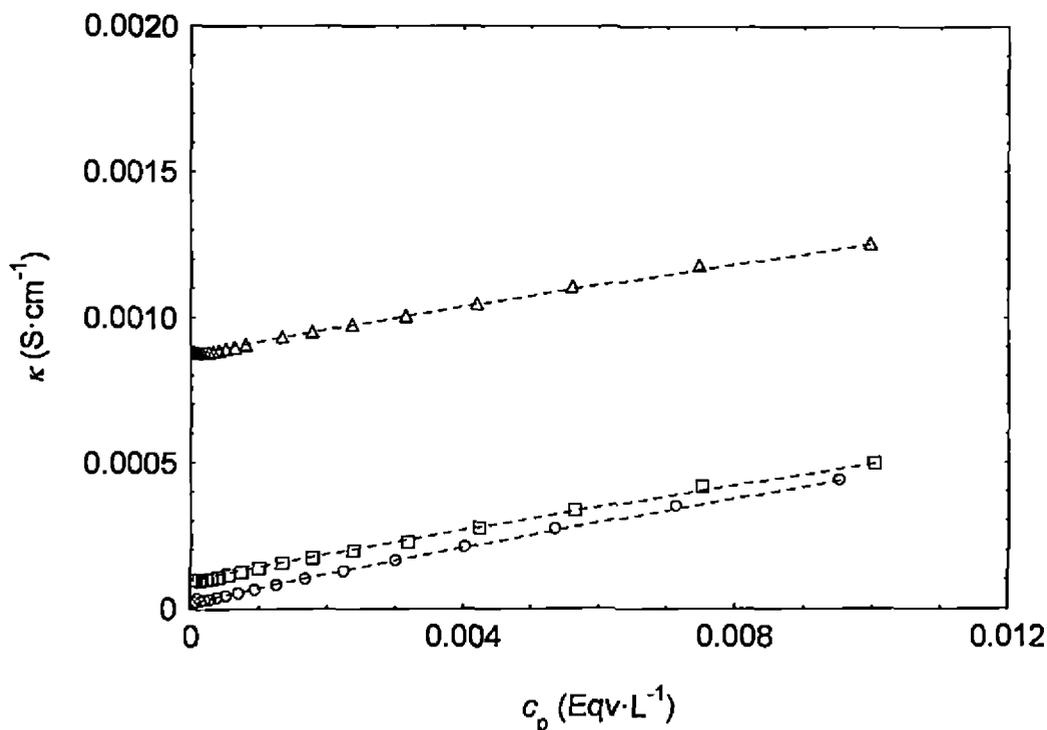


Figure 6.4 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 313.15 K in a 2-ethoxyethanol–water mixture with 25 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

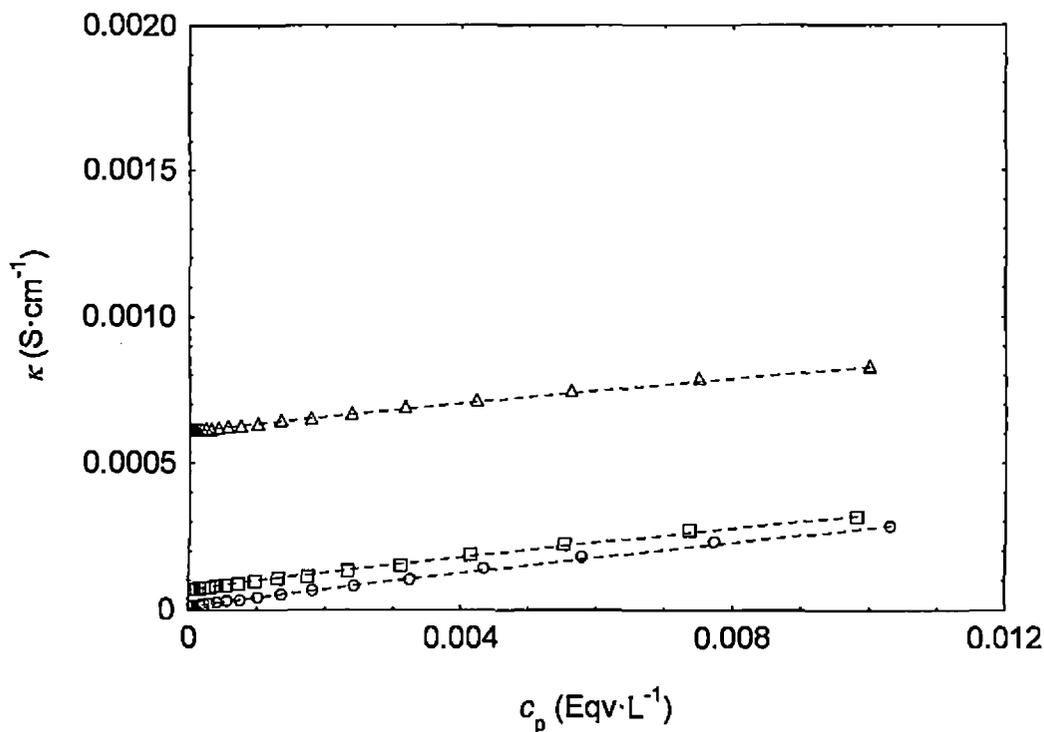


Figure 6.5 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 313.15 K in a 2-ethoxyethanol–water mixture with 40 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

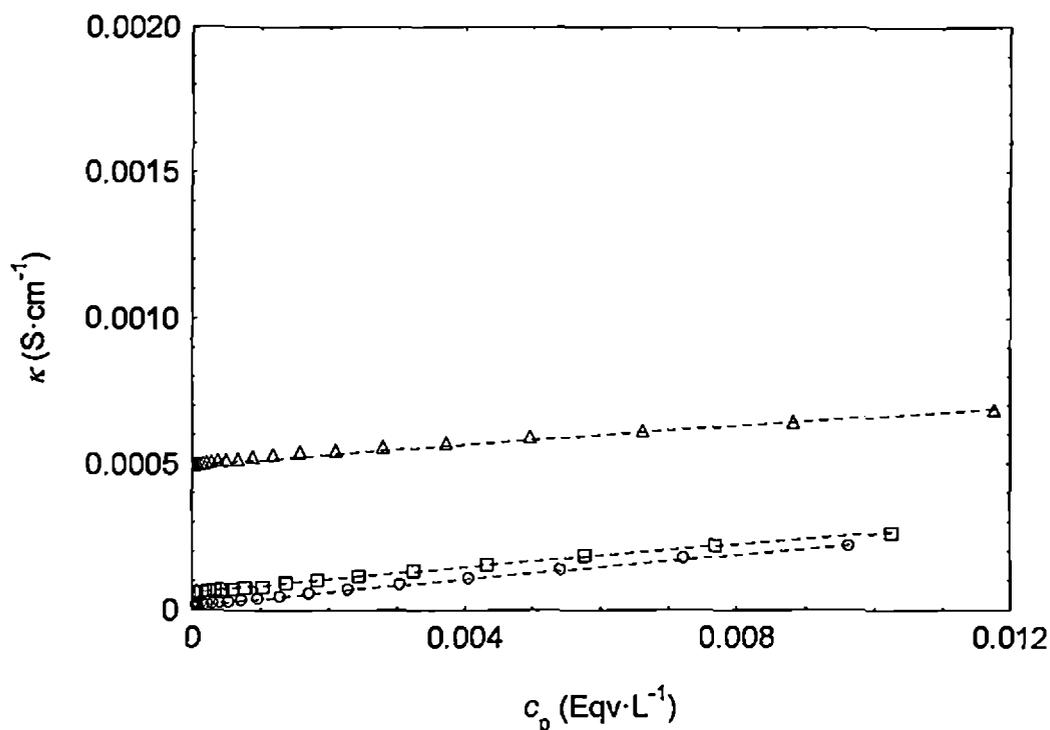


Figure 6.6 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 313.15 K in a 2-ethoxyethanol–water mixture with 50 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

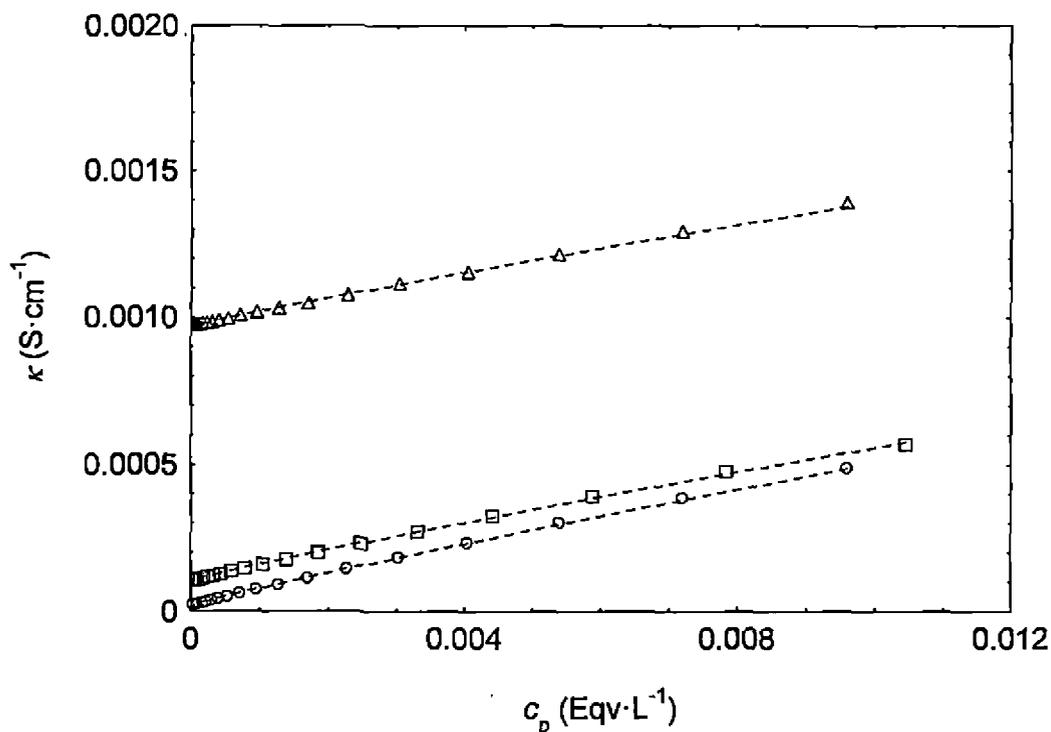


Figure 6.7 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 318.15 K in a 2-ethoxyethanol–water mixture with 25 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) mol·L⁻¹ NaCl respectively (see text).

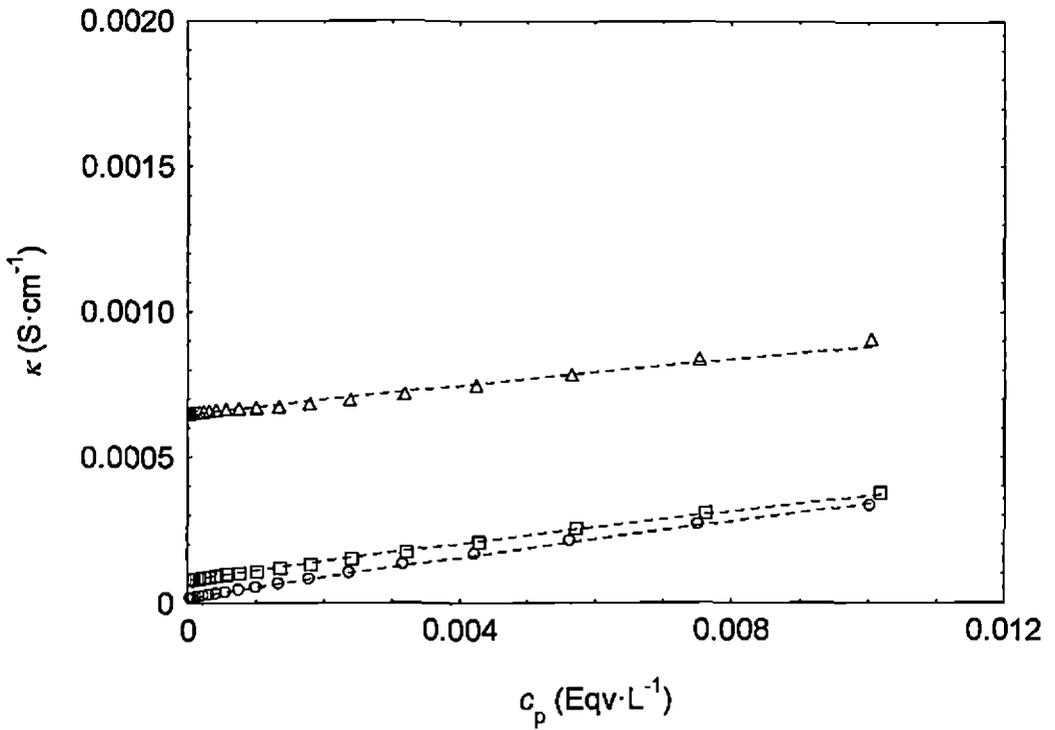


Figure 6.8 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 318.15 K in a 2-ethoxyethanol–water mixture with 40 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

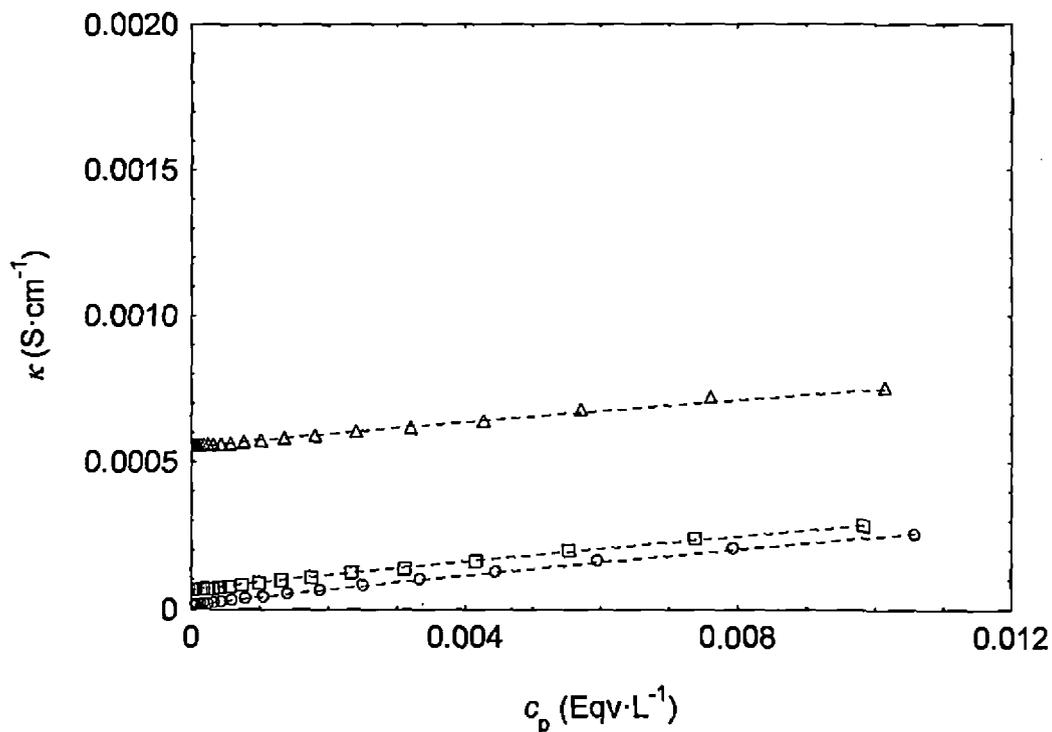


Figure 6.9 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 318.15 K in a 2-ethoxyethanol–water mixture with 50 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

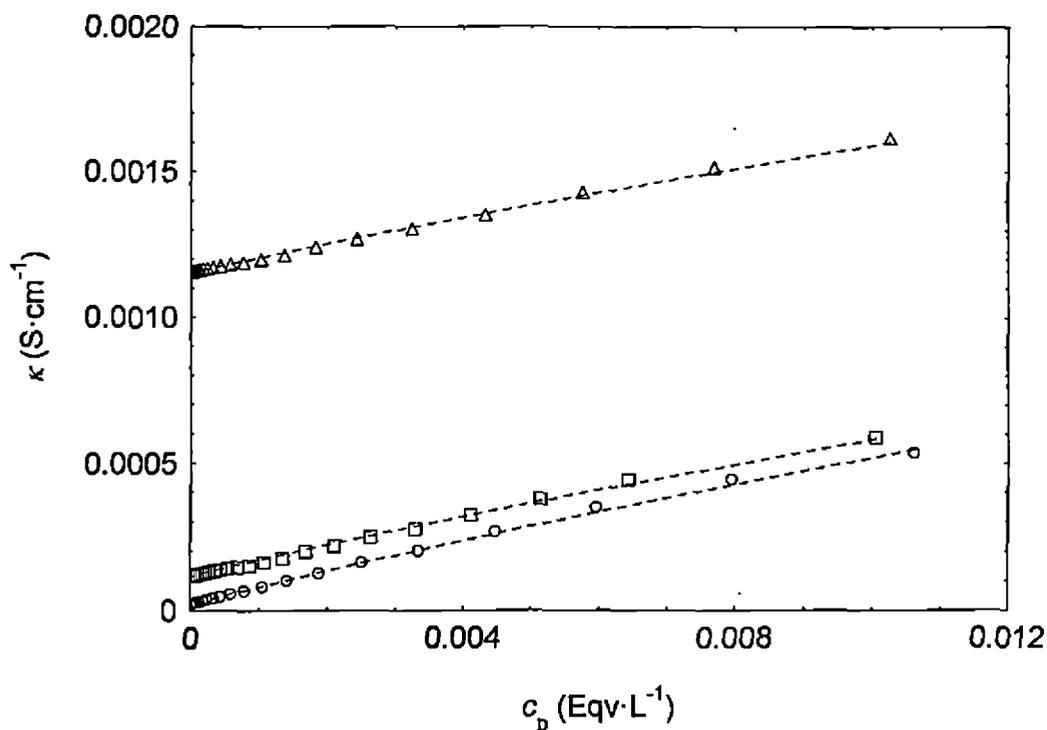


Figure 6.10 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 323.15 K in a 2-ethoxyethanol–water mixture with 25 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) $\text{mol} \cdot \text{L}^{-1}$ NaCl respectively (see text).

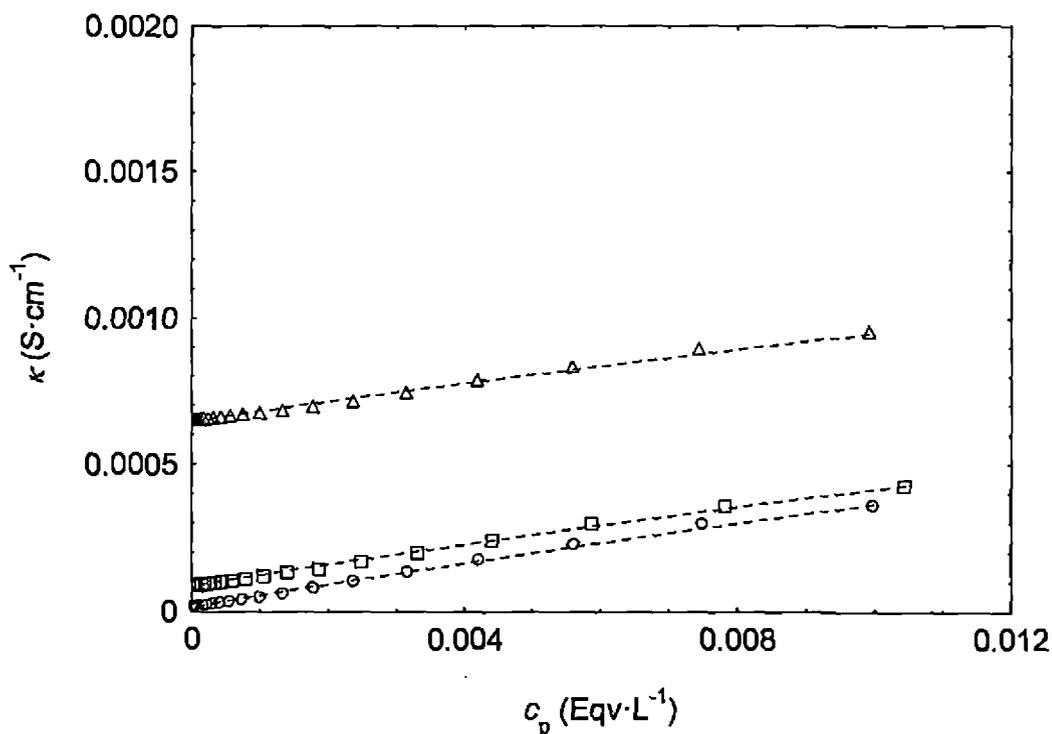


Figure 6.11 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 323.15 K in a 2-ethoxyethanol–water mixture with 40 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) mol·L⁻¹ NaCl respectively (see text).

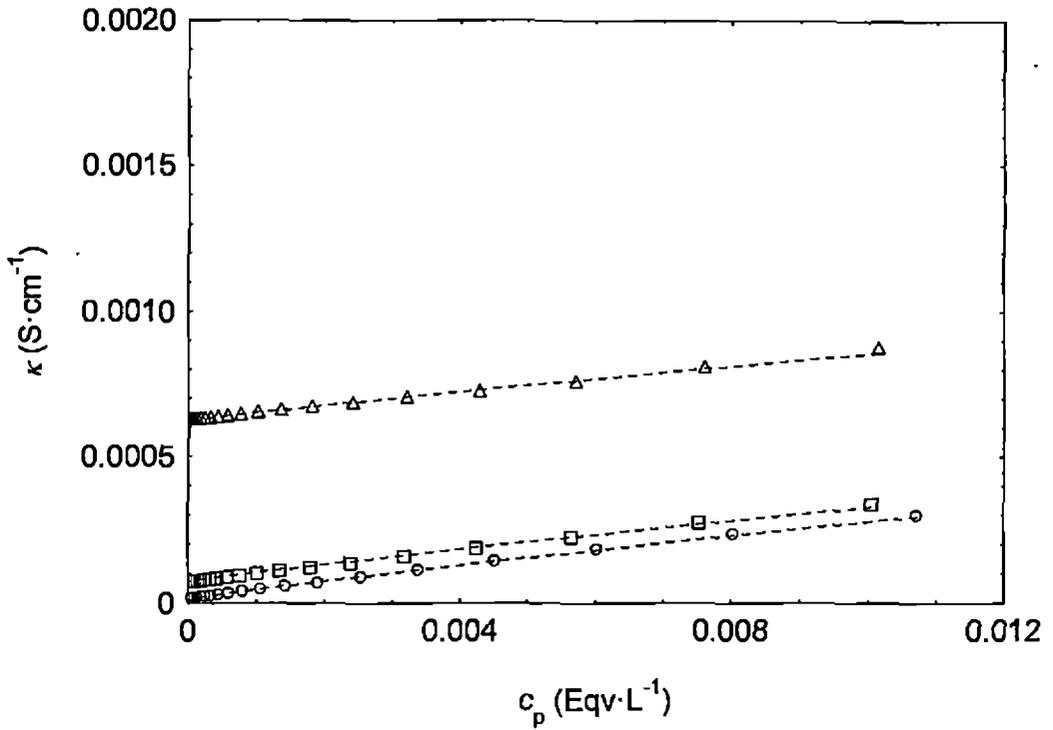


Figure 6.12 Specific conductivities (κ) of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at 323.15 K in a 2-ethoxyethanol–water mixture with 50 mass percent of 2-ethoxyethanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles, squares and triangles represent the polyelectrolyte solutions in presence of (1×10^{-4} , 1×10^{-3} , and 1×10^{-2}) mol·L⁻¹ NaCl respectively (see text).

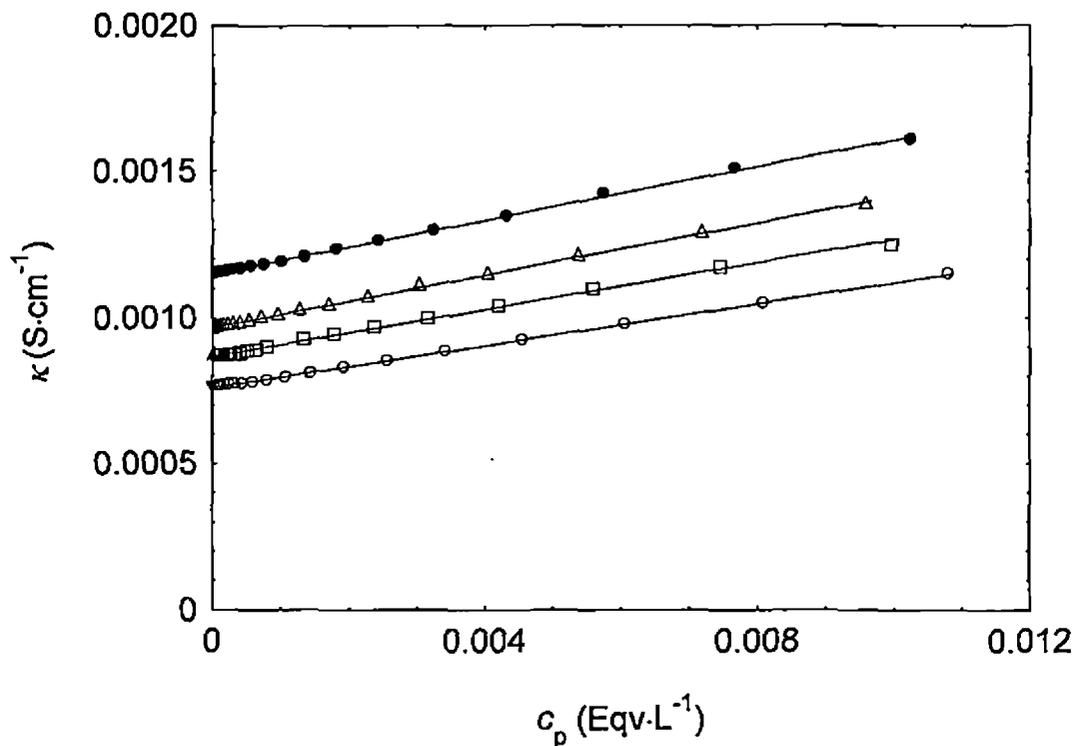


Figure 6.13 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (△) and 323.15 K (●) in a 2-ethoxyethanol–water mixture with 25 mass percent of 2-ethoxyethanol in the presence of $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ NaCl. Lines are used to guide the eye.

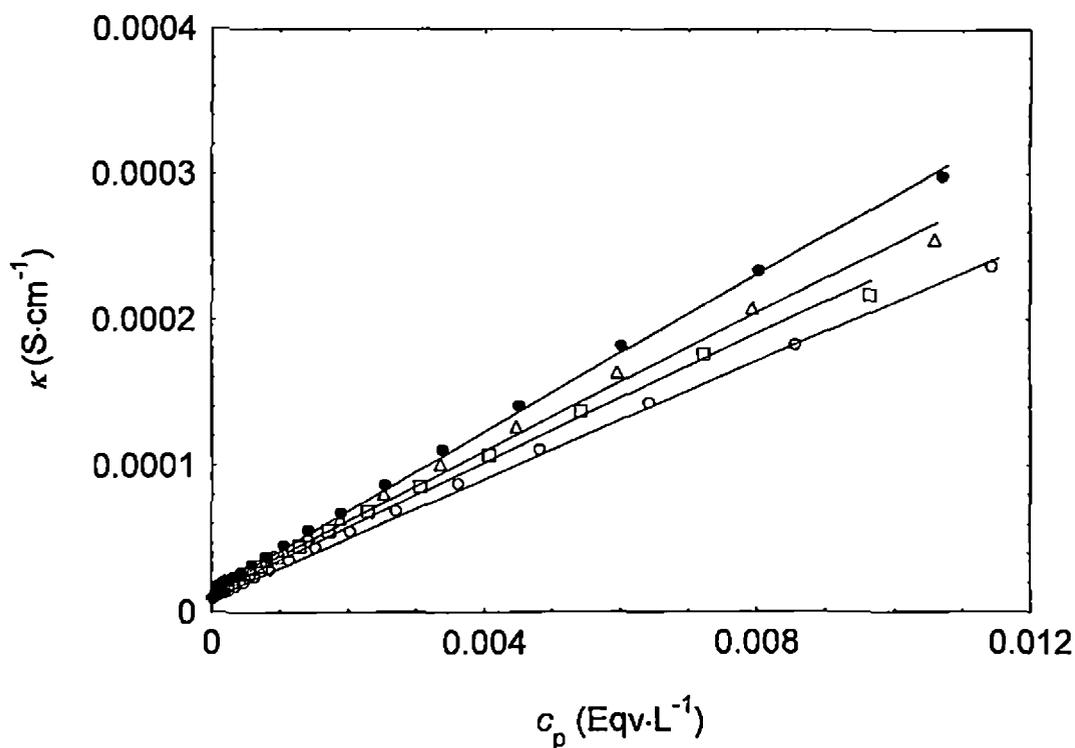


Figure 6.14 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 313.15 K (◻), 318.15 K (Δ) and 323.15 K (●) in a 2-ethoxyethanol–water mixture with 50 mass percent of 2-ethoxyethanol in the presence of $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ NaCl. Lines are used to guide the eye.

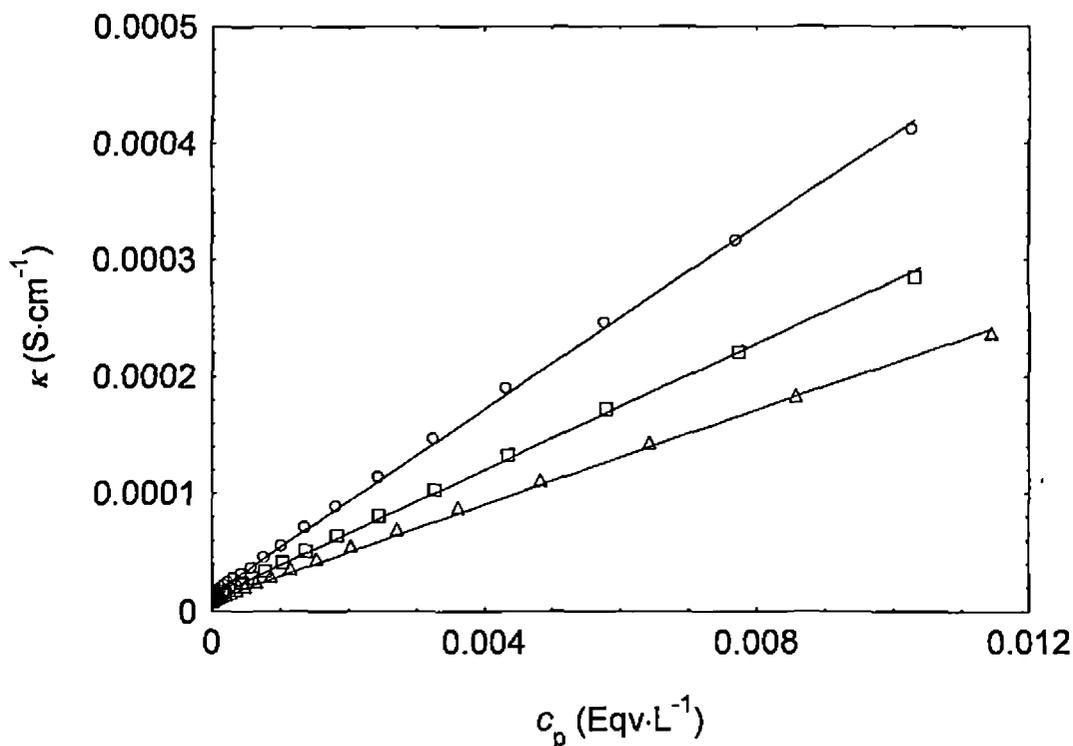


Figure 6.15 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 308.15 K in a 2-ethoxyethanol–water mixture with 25 (\circ), 40 (\square) and 50 (Δ) mass percent of 2-ethoxyethanol in the presence of 1×10^{-4} mol·L⁻¹ NaCl. Lines are used to guide the eye.

Chapter 7

Intrinsic Viscosities of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media Using the Isoionic Dilution Method

7.1 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 behaviour 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.¹⁻⁴ 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 (η_{sp}/c_p ; η_{sp} = specific viscosity and c_p = polymer concentration) varies linearly with concentration c_p in dilute solutions which led Huggins to propose the following equation^{2,5}

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

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behaviour 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 η_{sp}/c_p vs. c_p values to $c_p = 0$. On the other hand, the reduced viscosity of salt-free polyelectrolyte solutions exhibits an anomalous behaviour.

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.^{6,7} In

these studies, which are summarized in the pioneering work of Fuoss,^{6,7} 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 behaviour revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum, and normal polymer behaviour 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 η_{sp}/c_p vs. c_p 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^{8,9} 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, *i.e.*, at each of the polyelectrolyte concentration where isoionic dilution were performed. 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.⁸⁻¹³

The principal objective of the present contribution is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium polystyrenesulphonate in aqueous and binary aqueous 2-ethoxyethanol mixed solvent media. Further, the influences of the medium and the total ionic strength on the counterion condensation behaviour and on the changes in the conformation, if any, of the polyion will also be investigated.

7.2 Experimental

Sodium polystyrenesulphonate was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was *ca.* 70000 and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

2-Ethoxyethanol (G.R.E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity as $1.8277 \text{ mPa}\cdot\text{s}$ at 298.15 K ; these values are in good agreement with the literature values.¹⁴ For the preparation of the mixed solvents, triply distilled water with a specific conductance less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 308.15 K was used.

The viscometric measurements were performed at the experimental temperature using a Schultz-Immergut-type viscometer¹⁵ 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 $\pm 0.01 \text{ K}$ 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.^{16,17} 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

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

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.

7.3 Results and Discussion

7.3.1 Dependence of Reduced Viscosity with Polyelectrolyte Concentration

The typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free sodium polystyrenesulphonate solution in water at 308.15 K and in 2-ethoxyethanol–water mixtures containing 10 mass percent of 2-ethoxyethanol at 318.15 K are shown in Figures 1 and 2 respectively. In the absence of an added salt, the reduced viscosity is found to increase as the polyelectrolyte concentration decreases, for all the systems investigated here, bending up at low concentrations thus manifesting the typical polyelectrolyte behaviour. No maximum was, however, detected in the η_{sp}/c_p versus c_p profiles within the concentration range studied here.

7.3.2. Isoionic Dilution

Isoionic dilution was proposed to avoid the conformational change of the polyion thus eliminating the anomalous polyelectrolyte behaviour and to determine the intrinsic viscosity of the polyelectrolyte solution.⁸⁻¹³ Since intrinsic viscosity is a parameter which enables characterization of dimension and configuration of a polymer, this may play a crucial role in the discussion of polyelectrolyte behaviour in dilute solutions.

We have performed isoionic dilution on sodium polystyrenesulphonate solutions at three different polyelectrolyte concentrations (0.0033, 0.0054 and 0.0080 Eqv·L⁻¹) using NaCl in water and in four 2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at 308.15, 313.15, 318.15 and 323.15 K. The representative figures (Figures 1

and 2) also include the experimental data for isoionic dilution for the three different polyelectrolyte concentrations.

The reduced viscosity values as functions of polyelectrolyte concentration resulting from the isoionic dilution are found to decrease linearly as we lower the polyelectrolyte concentration and hence extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength using the well-known Huggins equation^{2,5} [Eq. (1)].

From the present experimental η_{sp}/c_p versus c_p data, the intrinsic viscosities and the Huggins constants have been determined by the method of least-squares using Eq. (1) and these are listed in Table 7.1.

7.3.3. Solvodynamic and Thermodynamic Behaviour

From Table 7.1 and Figures 7.3 to 7.8, it is apparent that the intrinsic viscosities and the Huggins constants for the present polyelectrolyte system vary with the total ionic strength, the medium and the experimental temperature. This observation, thus, indicates that the polyelectrolyte sodium polystyrenesulphonate differs quite appreciably in its solvodynamic and thermodynamic behaviours under varying conditions.

7.3.3.1. Variation of the Intrinsic Viscosity with the Solvent Medium at a Given Temperature and a Given Polyelectrolyte Concentration

At a given temperature and at a given polyelectrolyte concentration, the intrinsic viscosities are found to decrease as the medium becomes richer in 2-ethoxyethanol (Table 7.1 and Figure 7.3). With the addition of 2-ethoxyethanol to water, the relative permittivity of the medium decreases which results in a greater counterion condensation onto the polyion chain as the medium becomes richer in 2-ethoxyethanol. Greater counterion condensation leads to a smaller effective charge on the polyion with a concomitant reduction in the size of the polyion.

7.3.3.2. Variation of Intrinsic Viscosity with Temperature in a Given Solvent Medium and a Given Polyelectrolyte Concentration

In a given solvent medium and at a given polyelectrolyte concentration, the intrinsic viscosity is found to decrease with increasing temperature (Table 1 and Figure 7.5). With the increase of temperature, an expansion of the polyion chain is expected. On the other hand, an increase in temperature should also cause a reduction in the relative permittivity of the medium

leading to a contraction of the polyion chain due to more counterion condensation. The present observation indicates that the later effect predominates over the former in controlling the intrinsic viscosity of the polyelectrolyte as a function of temperature in a given solvent medium.

7.3.3.3. Variation of Huggins Constant with Solvent Medium at a Given Temperature and a Given Polyelectrolyte Concentration

At a given temperature and at a given polyelectrolyte concentration, the Huggins constants are found to increase as the medium becomes richer in 2-ethoxyethanol (Table 7.1 and Figure 7.4). This clearly demonstrates that the solvent medium becomes poorer towards the polyelectrolyte with the addition of 2-ethoxyethanol to water at a given temperature and at a given polyelectrolyte concentration. This is consistent with the general view that high k_H values are the characteristics of the poor solvents.¹⁶

7.3.3.4. Variation of Huggins Constants with Temperature in a Given Solvent Medium and a Given Polyelectrolyte Concentration

In a given solvent medium and at a given polyelectrolyte concentration, the Huggins constant value are found to increase with increasing temperature (Table 7.1 and Figure 7.6). This is an indication of the fact that the medium becomes poorer with increasing temperature and is consistent with the view pointed out in section 7.3.3.3.

7.3.4. Temperature Dependence of the Huggins Constants

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 7.2.

7.4. Conclusions

The present investigation reported the precise measurements on the viscosities of the solutions of sodium polystyrenesulphonate in water and in four 2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at 308.15, 313.15, 318.15 and

323.15 K. The intrinsic viscosities of the polyelectrolyte solutions were obtained through isoionic dilution maintaining the total ionic strengths of the solutions at polyelectrolyte concentrations 0.0033, 0.0054, and 0.0080 Eqv·L⁻¹ with sodium chloride. The Huggins constants were also obtained from the experimental results. The influences of the medium and the temperature on the intrinsic viscosities as well as on the Huggins constants have been interpreted in order to elucidate the solvodynamic and thermodynamic interactions occurring in solution.

7.5 References

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Table 7.1 Intrinsic Viscosities $[\eta]$, Huggins Constants k_H , and the Correlation Coefficients of Fits (as r^2) of Sodium Polystyrenesulphonate in Water and 2-Ethoxyethanol–Water Mixtures Containing 10, 25, 40, and 50 mass percent of 2-Ethoxyethanol at the Polyelectrolyte Concentrations where Isoionic Dilution was performed at 308.15, 313.15, 318.15, and 323.15 K

T (K)	Mass % of Cosolvent	c_p (Eqv·L ⁻¹)	$[\eta]$ (L·Eqv ⁻¹)	k_H	r^2
308.15	0	0.0033	43.7 ± 0.3	4.52 ± 0.09	0.997
		0.0054	40.0 ± 0.2	1.68 ± 0.04	0.995
		0.0080	35.6 ± 0.3	1.02 ± 0.05	0.980
	10	0.0033	37.9 ± 0.1	6.08 ± 0.06	0.999
		0.0054	35.9 ± 0.2	2.28 ± 0.05	0.996
		0.0080	30.8 ± 0.1	1.45 ± 0.04	0.995
	25	0.0033	34.4 ± 0.3	7.52 ± 0.13	0.997
		0.0054	31.8 ± 0.1	2.83 ± 0.07	0.995
		0.0080	28.8 ± 0.2	1.46 ± 0.07	0.979
	40	0.0033	32.7 ± 0.2	7.61 ± 0.12	0.998
		0.0054	29.8 ± 0.2	3.05 ± 0.06	0.996
		0.0080	26.6 ± 0.3	1.59 ± 0.11	0.963
50	0.0033	31.7 ± 0.2	7.65 ± 0.18	0.996	
	0.0054	26.8 ± 0.4	3.69 ± 0.21	0.974	
	0.0080	24.4 ± 0.2	1.81 ± 0.07	0.988	
313.15	0	0.0033	41.2 ± 0.2	5.15 ± 0.07	0.999
		0.0054	38.9 ± 0.2	1.78 ± 0.04	0.996
		0.0080	34.1 ± 0.2	1.13 ± 0.04	0.990
	10	0.0033	36.8 ± 0.2	6.51 ± 0.09	0.998
		0.0054	34.5 ± 0.2	2.38 ± 0.06	0.995
		0.0080	30.0 ± 0.2	1.52 ± 0.05	0.990
	25	0.0033	33.7 ± 0.3	7.89 ± 0.17	0.996
		0.0054	31.2 ± 0.2	3.00 ± 0.06	0.997
		0.0080	28.2 ± 0.3	1.57 ± 0.06	0.986
	40	0.0033	31.5 ± 0.3	7.94 ± 0.19	0.996
		0.0054	28.7 ± 0.2	3.11 ± 0.08	0.994
		0.0080	25.6 ± 0.2	1.62 ± 0.09	0.986
50	0.0033	30.2 ± 0.3	7.99 ± 0.19	0.995	
	0.0054	25.9 ± 0.2	3.73 ± 0.09	0.996	
	0.0080	23.4 ± 0.1	1.90 ± 0.05	0.994	
318.15	0	0.0033	39.3 ± 0.1	5.83 ± 0.06	0.999
		0.0054	37.4 ± 0.2	2.01 ± 0.06	0.993
		0.0080	32.8 ± 0.2	1.25 ± 0.05	0.985
	10	0.0033	35.7 ± 0.2	6.87 ± 0.10	0.998
		0.0054	33.4 ± 0.2	2.57 ± 0.06	0.996
		0.0080	29.2 ± 0.3	1.64 ± 0.08	0.980

Table 7.1 (Continued)

T (K)	Mass % of Cosolvent	c_p (Eqv·L ⁻¹)	$[\eta]$ (L·Eqv ⁻¹)	k_H	r^2	
323.15	25	0.0033	32.4 ± 0.3	7.93 ± 0.30	0.989	
		0.0054	30.7 ± 0.2	3.08 ± 0.06	0.995	
		0.0080	27.0 ± 0.1	1.66 ± 0.07	0.985	
	40	0.0033	31.0 ± 0.3	7.97 ± 0.15	0.997	
		0.0054	28.0 ± 0.3	3.22 ± 0.10	0.992	
		0.0080	25.1 ± 0.2	1.68 ± 0.08	0.982	
	50	0.0033	28.9 ± 0.3	8.07 ± 0.22	0.994	
		0.0054	24.8 ± 0.3	3.88 ± 0.15	0.989	
		0.0080	21.9 ± 0.1	2.15 ± 0.06	0.994	
	0	0	0.0033	38.1 ± 0.3	5.93 ± 0.12	0.997
			0.0054	35.9 ± 0.2	2.08 ± 0.06	0.993
			0.0080	31.3 ± 0.2	1.32 ± 0.05	0.987
		10	0.0033	34.1 ± 0.2	6.89 ± 0.14	0.997
			0.0054	32.1 ± 0.2	2.60 ± 0.08	0.992
			0.0080	28.0 ± 0.2	1.65 ± 0.04	0.994
		25	0.0033	31.1 ± 0.3	7.98 ± 0.16	0.997
			0.0054	30.3 ± 0.1	3.18 ± 0.05	0.997
			0.0080	26.7 ± 0.2	1.70 ± 0.08	0.984
	40	0.0033	30.2 ± 0.3	8.05 ± 0.15	0.997	
		0.0054	27.3 ± 0.2	3.33 ± 0.09	0.994	
		0.0080	24.2 ± 0.2	1.91 ± 0.08	0.986	
	50	0.0033	27.6 ± 0.3	8.13 ± 0.24	0.995	
		0.0054	23.6 ± 0.2	3.91 ± 0.15	0.992	
		0.0080	20.7 ± 0.1	2.64 ± 0.06	0.996	

Table 7.2 Parameters of Eq. (2) and the Correlation Coefficients of Fits (as r^2) for Sodium Polystyrenesulphonate in Water, 10, 25, 40, and 50 mass percent 2-Ethoxyethanol–Water Mixtures

Mass % of Cosolvent	c_p (Eqv·L ⁻¹)	$\ln A$	B	r^2
0	0.0033	-4.25	-0.019	0.922
	0.0054	-4.18	-0.015	0.958
	0.0080	-5.36	-0.017	0.983
10	0.0033	-0.82	-0.008	0.890
	0.0054	-2.07	-0.009	0.938
	0.0080	-2.48	-0.009	0.922
25	0.0033	0.90	-0.004	0.759
	0.0054	-1.27	-0.007	0.967
	0.0080	-2.77	-0.010	0.956
40	0.0033	0.98	-0.003	0.803
	0.0054	-0.73	-0.006	0.986
	0.0080	-3.17	-0.012	0.840
50	0.0033	0.86	-0.004	0.832
	0.0054	-0.01	-0.004	0.925
	0.0080	-7.19	-0.025	0.928

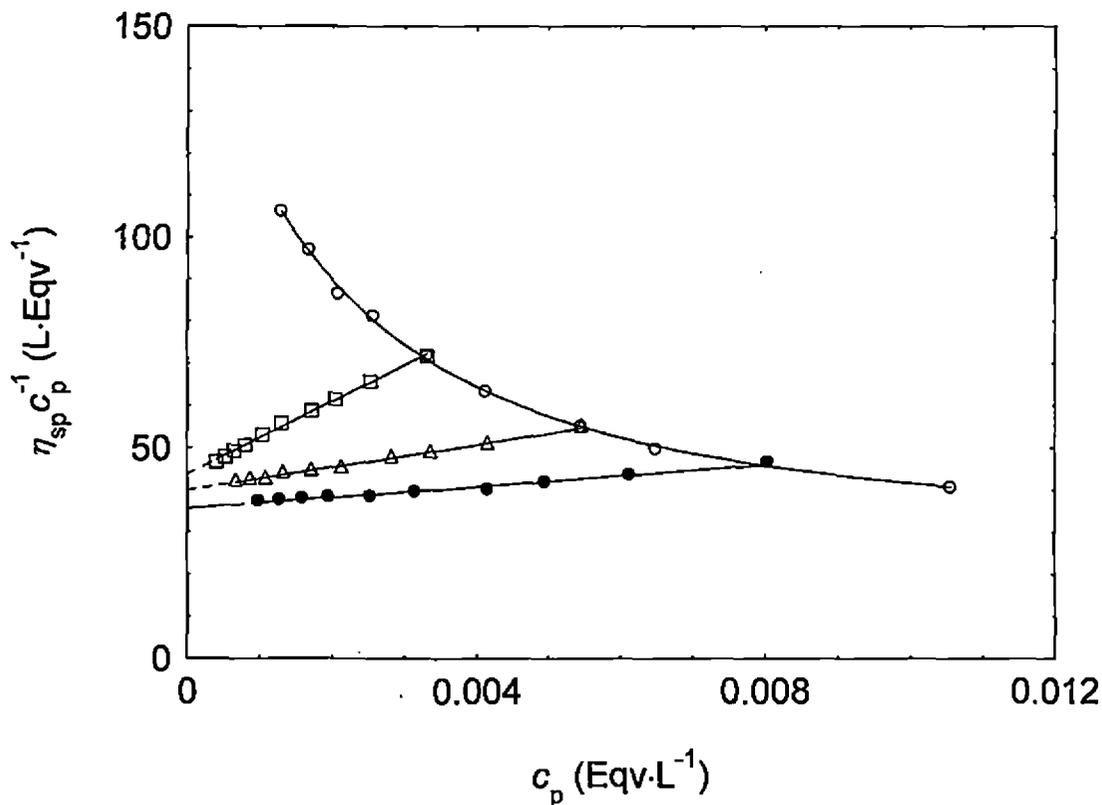


Figure 7.1 The variation of the reduced viscosity for sodium polystyrenesulphonate with polyelectrolyte concentration in water at 308.15 K (○). Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with constant total ionic strengths at polyelectrolyte concentrations 0.0033 (□), 0.0054 (Δ), and 0.0080 (●) Eqv·L⁻¹.

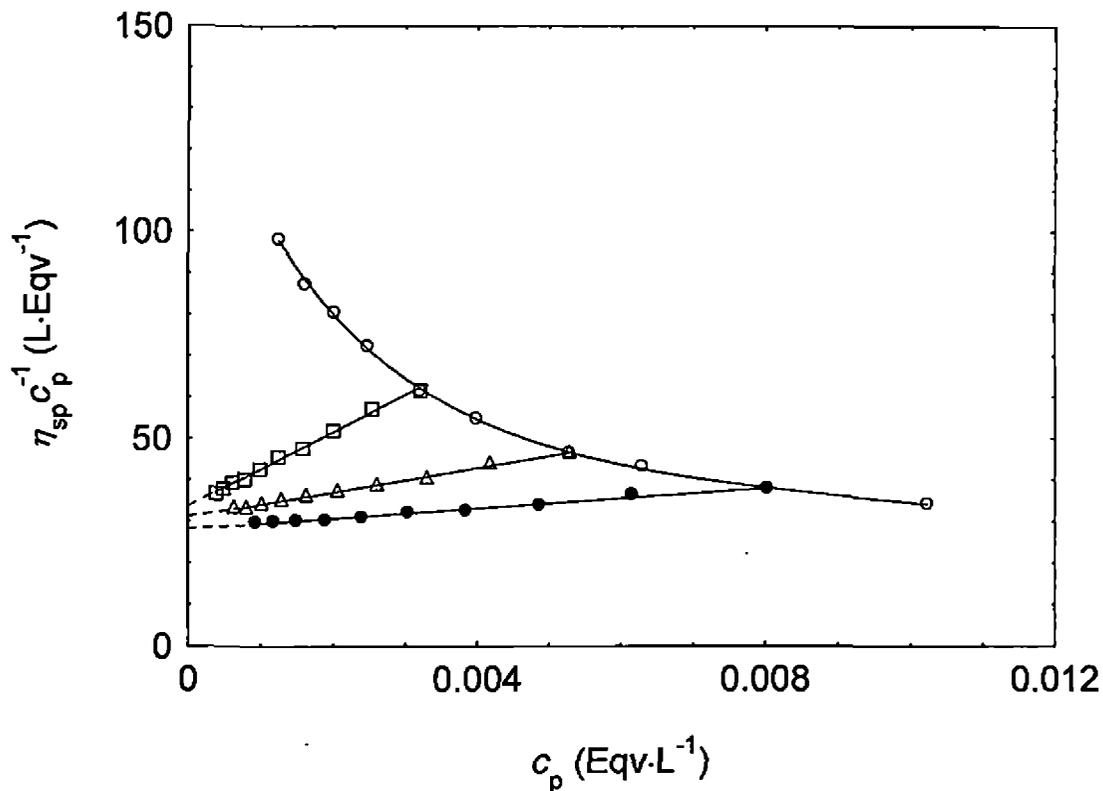


Figure 7.2 The variation of the reduced viscosity for sodium polystyrenesulphonate with polyelectrolyte concentration in 2-ethoxyethanol–water mixture containing 25 mass percent 2-ethoxyethanol at 313.15 K (○). Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with total ionic strengths 0.0033 (□), 0.0054 (Δ), and 0.0080 (●) Eqv·L⁻¹.

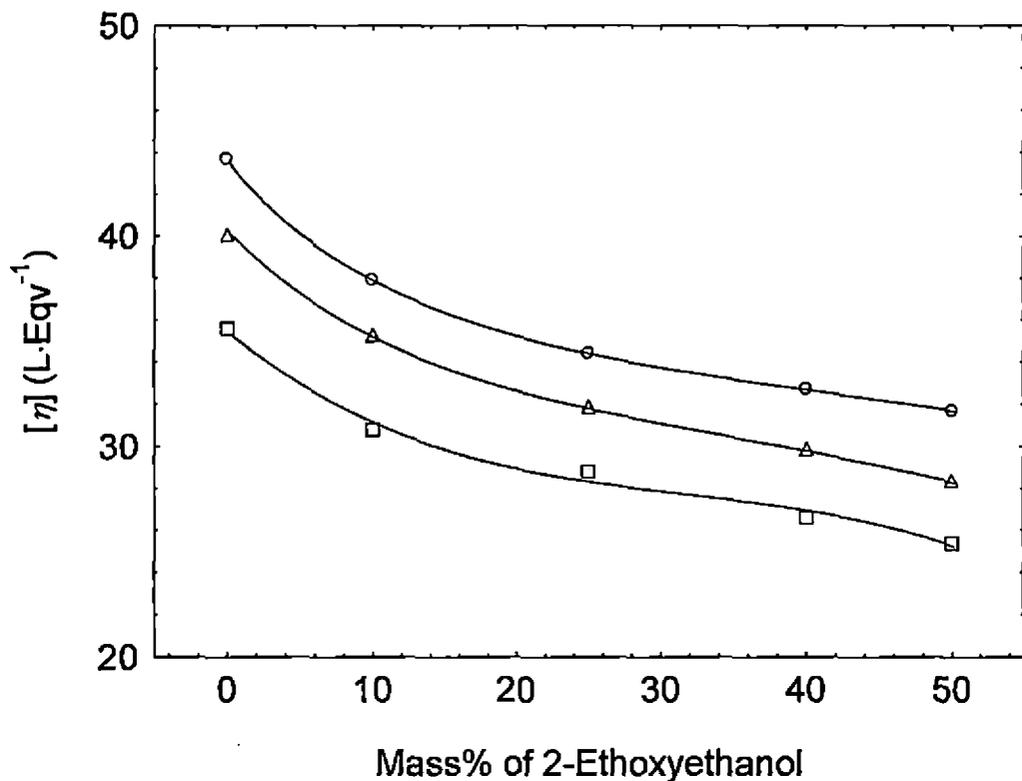


Figure 7.3 The effect of medium on the intrinsic viscosity of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media at 308.15 K obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (Δ), and 0.0080 (□) Eqv·L⁻¹.

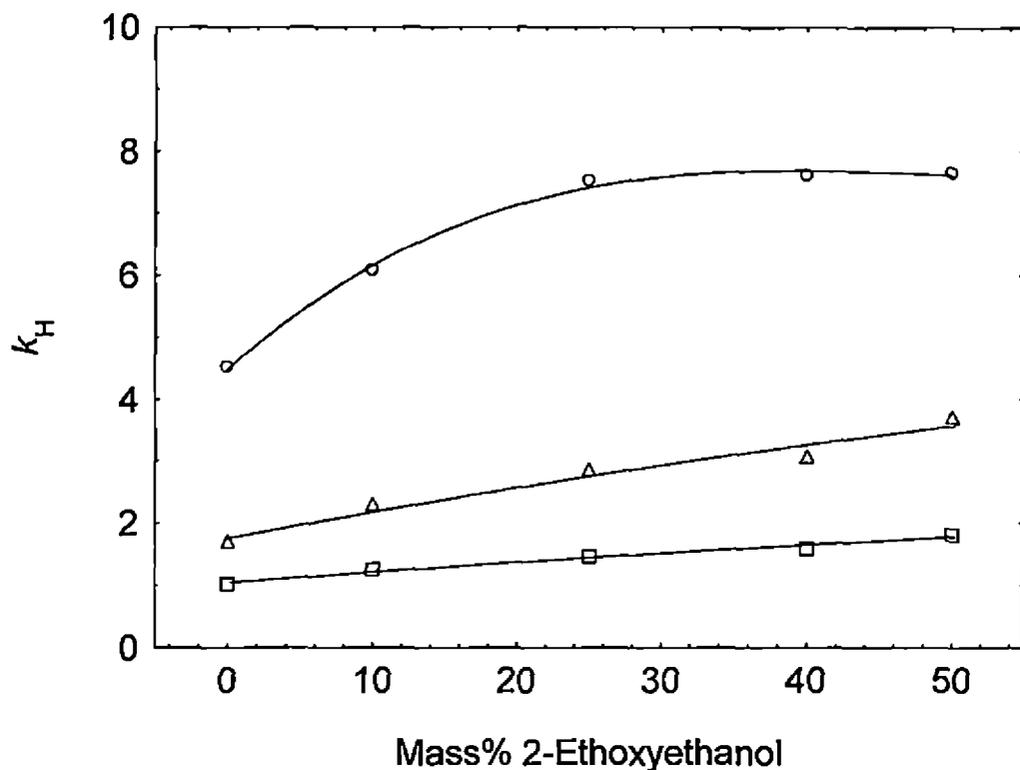


Figure 7.4 The effect of medium on the Huggins constant of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media at 308.15 K obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (Δ), and 0.0080 (□) Eqv·L⁻¹.

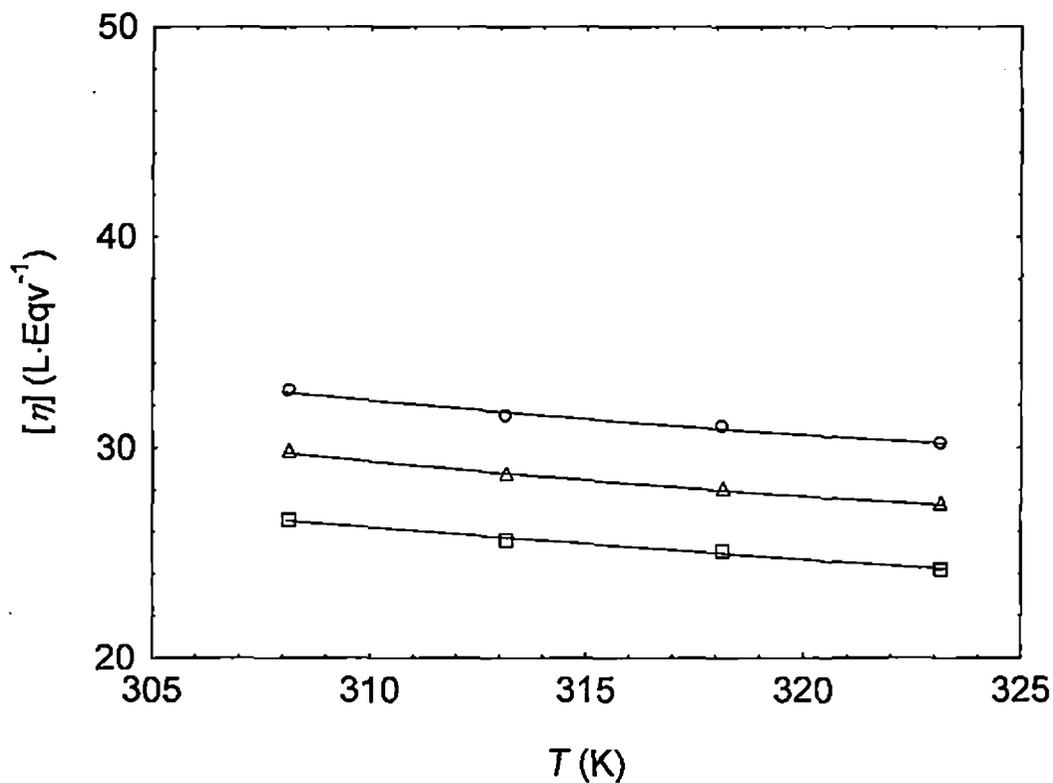


Figure 7.5 The effect of temperature on the intrinsic viscosity of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixed solvent media obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (Δ), and 0.0080 (□) Eqv·L⁻¹.

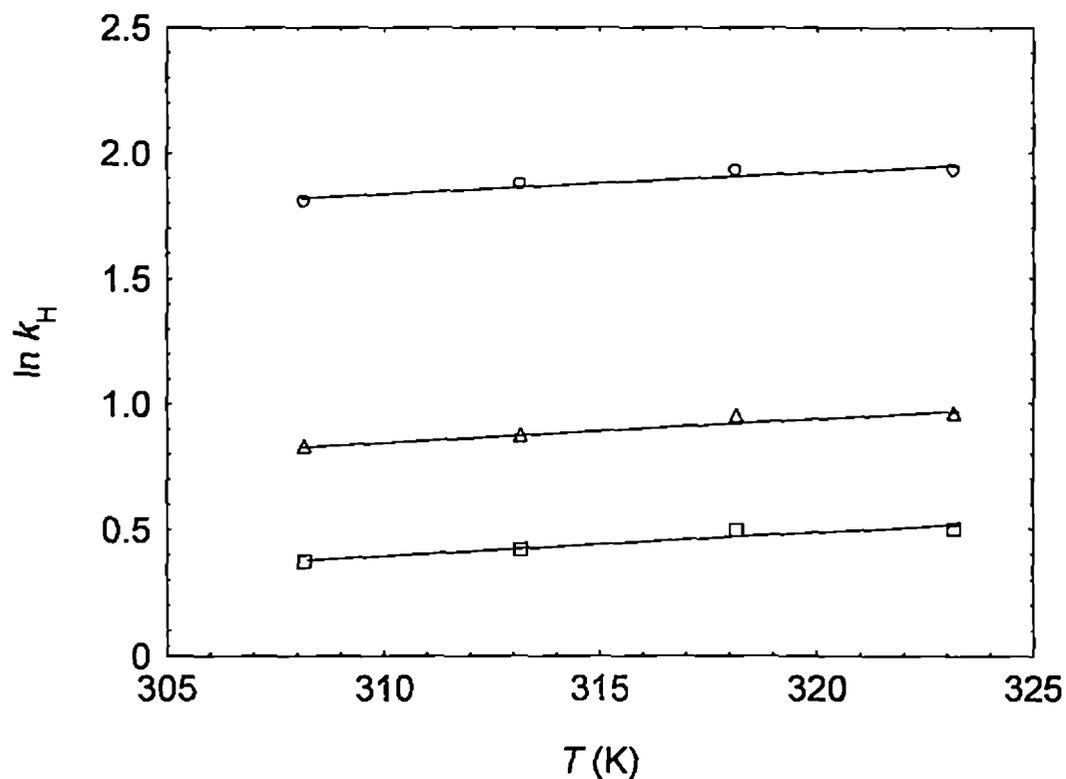


Figure 7.6 The effect of temperature on the Huggins constant of sodium polystyrenesulphonate in 10 mass percent 2-ethoxyethanol–water mixed solvent media obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (Δ), and 0.0080 (□) Eqv·L⁻¹

Chapter 8

Viscosities of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media in Presence of an Electrolyte

8.1 Introduction

As described in the previous chapter, 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. 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^{1,2}

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

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behaviour of the polymer molecules in solution, c_p 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 sodium polystyrenesulphonate in water as well as in 2-ethoxyethanol–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, provided there is an excess of low-molar-mass electrolyte, at a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity (η_{sp} / c_p) varies linearly with the polymer concentration (c_p) similar to that for a neutral macromolecular solution, thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation.^{1,2}

This chapter describes the viscometric behaviour of sodium polystyrenesulphonate in absence and also in presence of an electrolyte (NaCl) in 2-ethoxyethanol–water mixed solvent media. Our objective is to focus on the role of electrostatic interactions on the viscosity of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media. The intrinsic viscosities of sodium polystyrenesulphonate in these mixtures have also been determined.

8.2 Experimental

2-Ethoxyethanol (G.R.E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g.cm}^{-3}$ and a co-efficient of viscosity of 1.8277 mPa.s at 298.15 K ; these values are in good agreement with the literature values.³ Triply distilled water with a specific conductance less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The sodium salt of polystyrenesulphonic acid employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was 70000 with a degree of substitution (DS) of 1.0 , and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

The viscometric measurements were performed at 308.15 , 313.15 , 318.15 and 323.15 K using a Schultz-Immergut-type viscometer⁴ 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 $\pm 0.01 \text{ K}$ of the desired temperature by means of a mercury-in-glass thermo regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.^{5,6} 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 thus confirming the shear rate independence of the reduced viscosity values in the present study.

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

8.3 Results and Discussion

We have measured the variation of reduced viscosity of sodium polystyrenesulphonate with polymer concentration in pure water as well as in

2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at four different temperatures namely 308.15, 313.15, 318.15 and 323.15 K.

In each of these cases the effect of varying concentration of an added salt (1×10^{-4} , 1×10^{-3} , 1×10^{-2} and 1×10^{-1} mol·L⁻¹ of NaCl) was also investigated.

8.3.1 Variation of Reduced Viscosity with Polyelectrolyte Concentration

Figures 8.1 to 8.10 show the typical dependence of the reduced viscosity with polyelectrolyte concentration for the investigated systems. In absence of added NaCl, the reduced viscosity is found to increase as polyelectrolyte concentration decreases bending up at low concentration. No maximum was, however, detected in the η_{sp}/c_p vs. c_p profiles within the concentration range studied here under salt-free conditions. Similar non-linear increase in the reduced viscosity values as the polyelectrolyte concentration is reduced was also observed in polyelectrolyte solutions containing 1.5×10^{-3} , 2.5×10^{-3} and 4.0×10^{-3} mol·L⁻¹ of NaCl (Figures 8.1 to 8.10). An increase in the added salt concentration resulted in the reduction in the absolute values of η_{sp}/c_p greatly. This is a characteristic behaviour of the viscosity of polyelectrolyte solutions. This large decrease in the reduced viscosity can be accounted for by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. Therefore, it is virtually impossible to obtain the intrinsic viscosity of the present polyelectrolyte solutions without added salt and also in the presence of a small amount of the added salt by the usual procedure of the extrapolation of the reduced viscosity versus concentration profiles to zero polyelectrolyte concentration.

8.3.2 Influence of Large Amount of Added Salt: Determination of Intrinsic Viscosity

When the added salt concentration is sufficiently high (1×10^{-1} mol·L⁻¹), 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 sodium polystyrenesulfonate in 2-ethoxyethanol–water mixed solvent media using the Huggins equation, Eq. (1).

From the present experimental η_{sp}/c vs. c_p 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 8.1 along with their standard errors and the correlation coefficients of fits (as r^2).

The intrinsic viscosities of sodium polystyrenesulphonate in water and in 2-ethoxyethanol–water mixtures in presence of $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ 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.*, at polyelectrolyte concentrations of 1.5×10^{-3} , 2.5×10^{-3} , and $4.0 \times 10^{-3} \text{ Eqv} \cdot \text{L}^{-1}$ (*cf.* Chapter 7). 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.

8.3.3 Influence of Medium on the Intrinsic Viscosity

The intrinsic viscosity values of sodium polystyrenesulphonate are found to decrease significantly as the solvent medium becomes richer in 2-ethoxyethanol at any given temperature. The relative permittivity of the medium decreases as more and more 2-ethoxyethanol is added to water (*cf.* Table 3.1, Chapter 3) and hence more counterion condensation takes place due to an improvement of polyion-counterion interactions. The polyion chain will thus have less effective charge as the medium gets richer in 2-ethoxyethanol, and this would facilitate coiling of the polyion chain and result in a reduction in the intrinsic viscosity values.

8.3.4 Influence of Temperature on the Intrinsic Viscosity

An increase in temperature leads to a decrease in the intrinsic viscosity values in water as well as in 2-ethoxyethanol–water mixtures. Increasing temperature causes desolvation of the counterions and this would result in more counterion condensation onto the polyion chains. Increasing temperature also causes a decrease in the relative permittivity of the medium thus favouring counterion condensation. These obviously result in the contraction of the polyions as a result of coiling. It might be noted that the effect of temperature on the intrinsic viscosities and the Huggins constants are less pronounced as compared to the effect of solvent composition.

8.4 Conclusions

The present chapter reported precise measurements on the viscosities of the solutions of sodium polystyrenesulphonate in water and in four 2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at 308.15, 313.15, 318.15 and

323.15 K in presence of varying concentration of added sodium chloride. The viscosity of the present system reveals the characteristic behaviour of polyelectrolyte solutions. Both in the absence and in the presence of small amount of an added salt (1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol·L⁻¹ NaCl), the reduced viscosity is found to increase as polymer concentration decreases bending up at low concentration. No maximum was, however, detected in the η_{sp}/c_p vs. c_p profiles within the concentration range studied in both the cases. Increasing the concentration of the added salt decreases the absolute value of η_{sp}/c_p greatly. 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 (1×10^{-1} M), regular neutral polymer behaviour is recovered thus enabling us to determine the intrinsic viscosity of sodium polystyrenesulphonate in water and in 2-ethoxyethanol–water mixed solvent media using the Huggins equation. The variations of the intrinsic viscosity with temperature and solvent medium have been interpreted in terms of the variation in the coiling of the polyion chain and counterion condensation.

8.5 References

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Table 8.1 Intrinsic Viscosities $[\eta]$, Huggins Constants k_H , and the Correlation Coefficients of Fits (as r^2) of Sodium Polystyrenesulphonate in Water, and in 2-Ethoxyethanol–Water Mixtures with 10, 25, 40 and 50 Mass Percent of 2-Ethoxyethanol in Presence of 1×10^{-1} mol·L⁻¹ of NaCl at 308.15, 313.15, 318.15 and 323.15 K

T (K)	Mass % of Cosolvent	$[\eta]$ L·Eqv ⁻¹	k_H	r^2
308.15	0	33.47	0.05	0.9282
	10	31.63	0.06	0.9677
	25	29.80	0.08	0.9236
	40	28.22	0.07	0.9832
	50	24.66	0.08	0.9783
313.15	0	32.79	0.06	0.8618
	10	30.89	0.06	0.9038
	25	29.23	0.05	0.9171
	40	27.57	0.10	0.9082
	50	23.96	0.06	0.9391
318.15	0	31.62	0.07	0.8645
	10	29.93	0.06	0.9597
	25	28.67	0.05	0.8489
	40	26.95	0.09	0.9561
	50	22.92	0.06	0.9960
323.15	0	29.92	0.08	0.8713
	10	29.21	0.06	0.9550
	25	27.89	0.06	0.9089
	40	26.03	0.10	0.9912
	50	22.72	0.06	0.9909

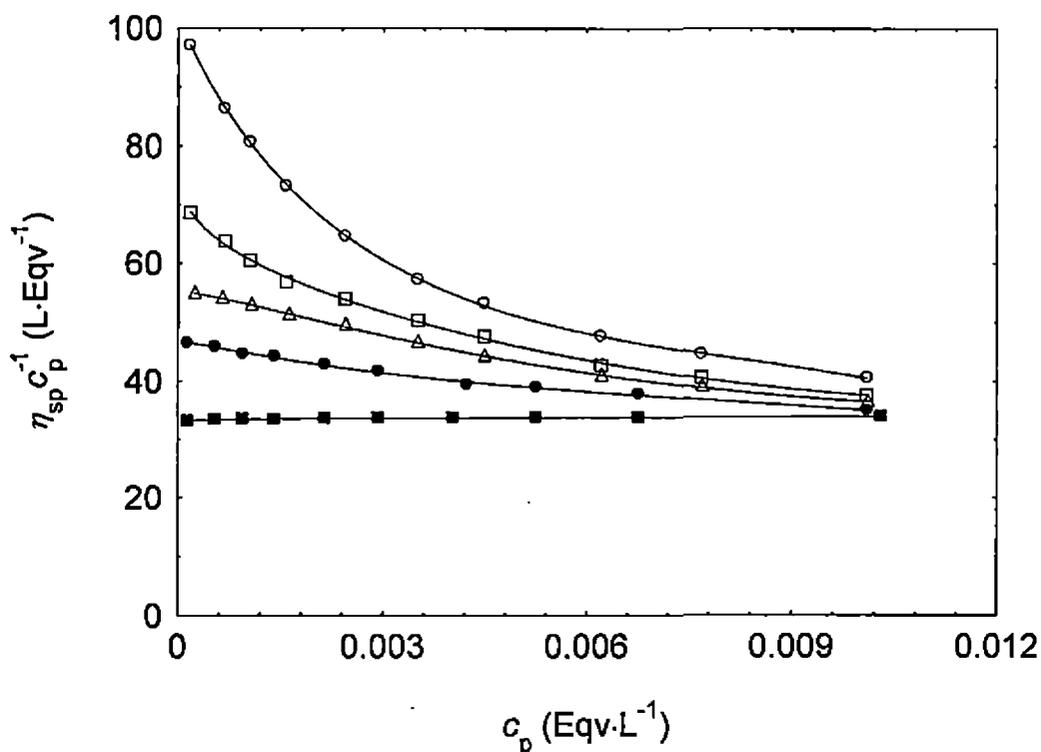


Figure 8.1 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in water at 308.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

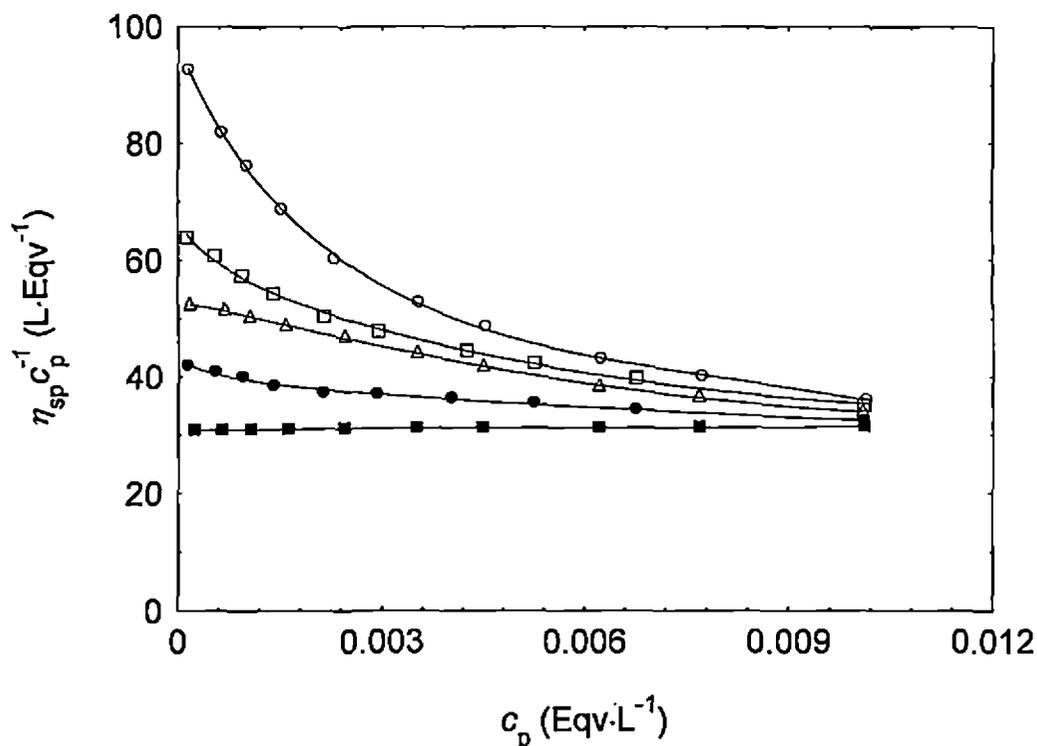


Figure 8.2 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 10 mass percent of 2-ethoxyethanol–water at 313.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

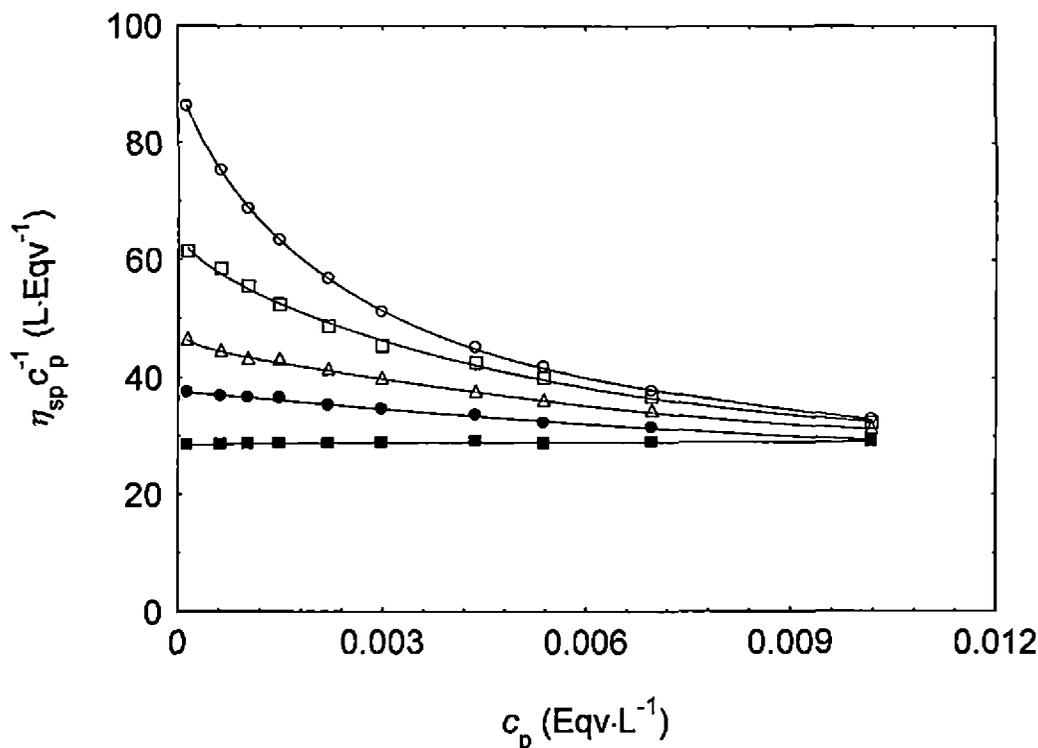


Figure 8.3 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 25 mass percent of 2-ethoxyethanol–water at 318.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

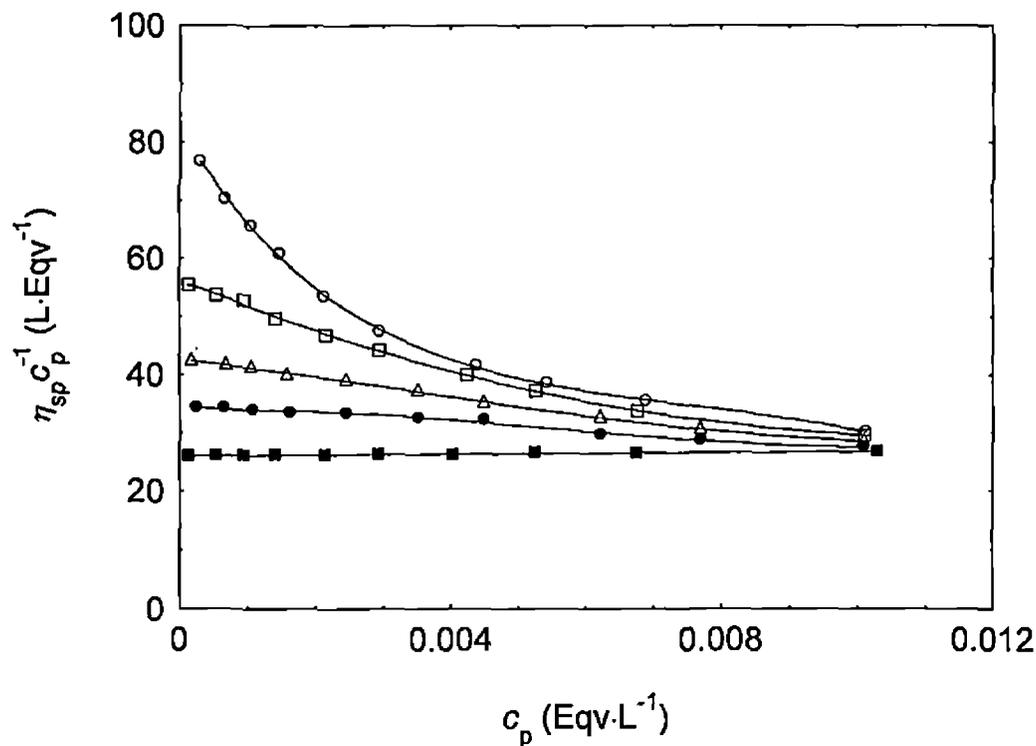


Figure 8.4 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 40 mass percent of 2-ethoxyethanol–water at 323.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

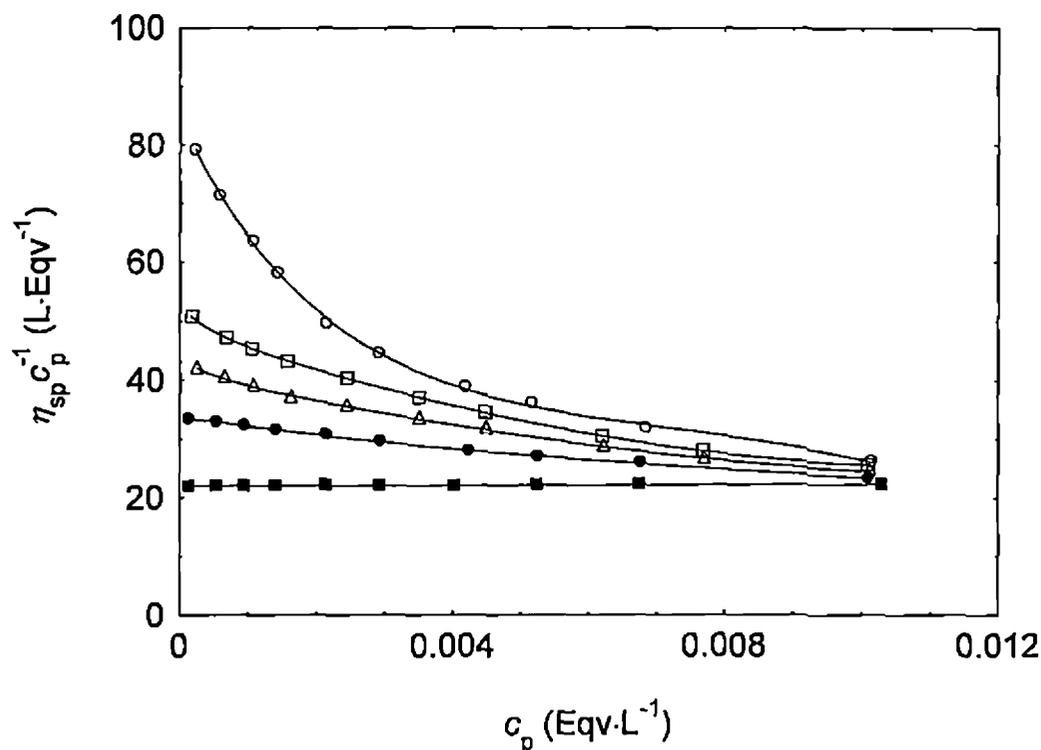


Figure 8.5 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 50 mass percent of 2-ethoxyethanol–water at 323.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

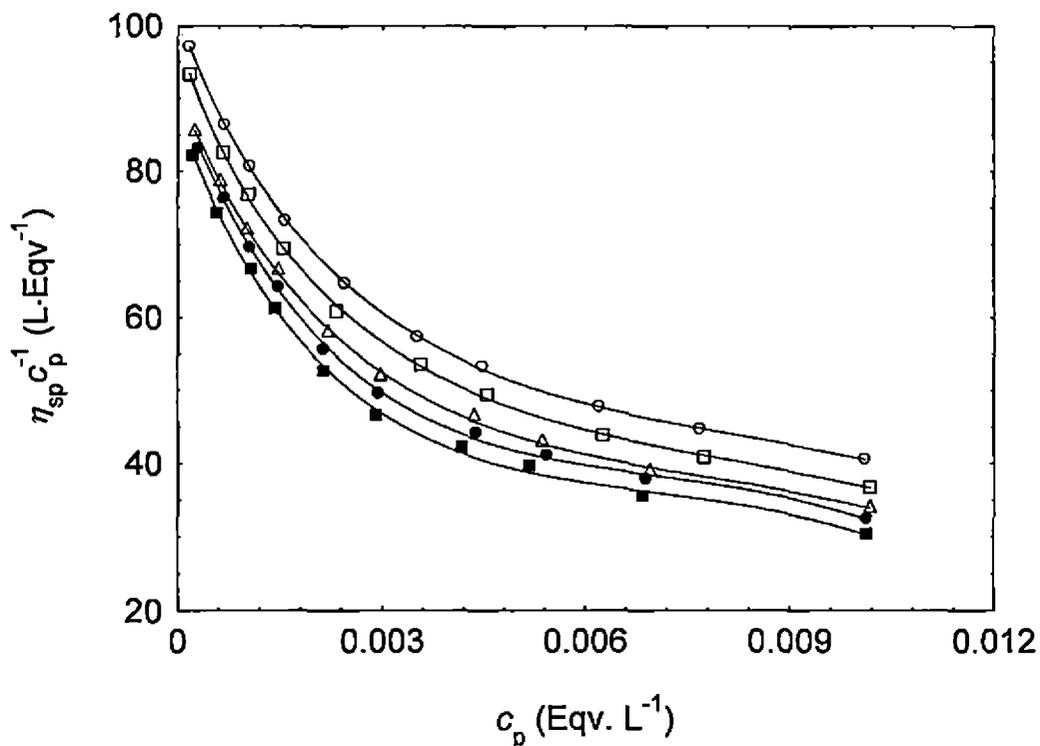


Figure 8.6 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 308.15 K in absence of added salt for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass per cent; triangle: 25 mass per cent; closed circle: 40 mass per cent and closed square: 50 mass per cent). Lines are used to guide the eye.

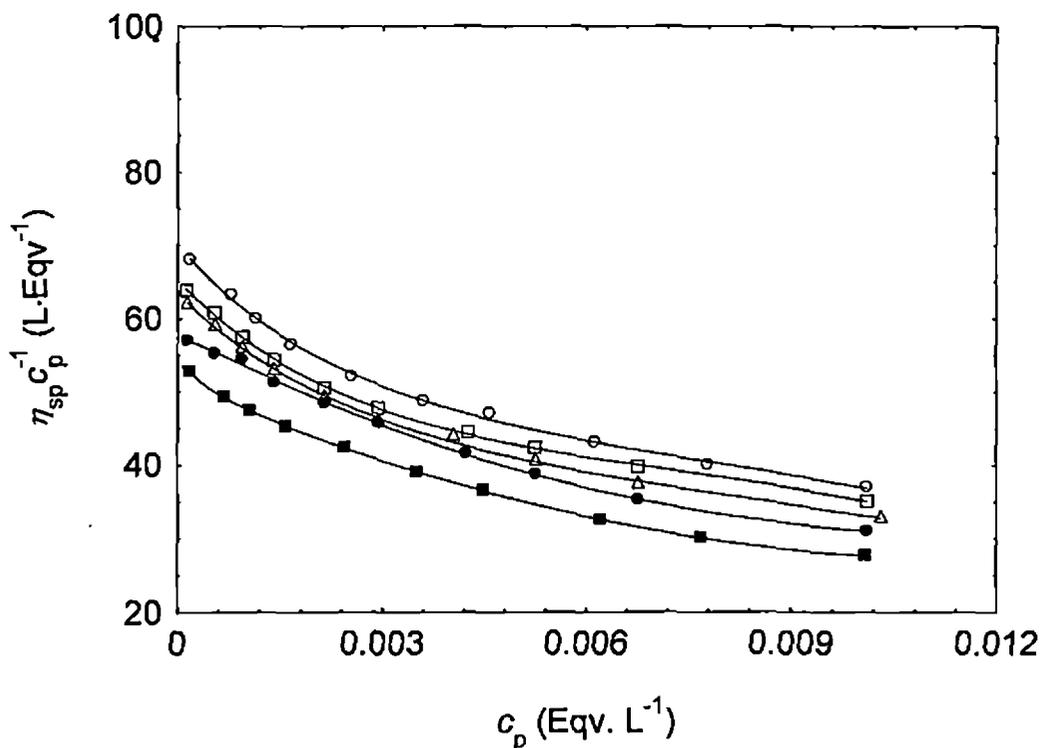


Figure 8.7 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp} / c_p) of sodium polystyrenesulphonate at 313.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

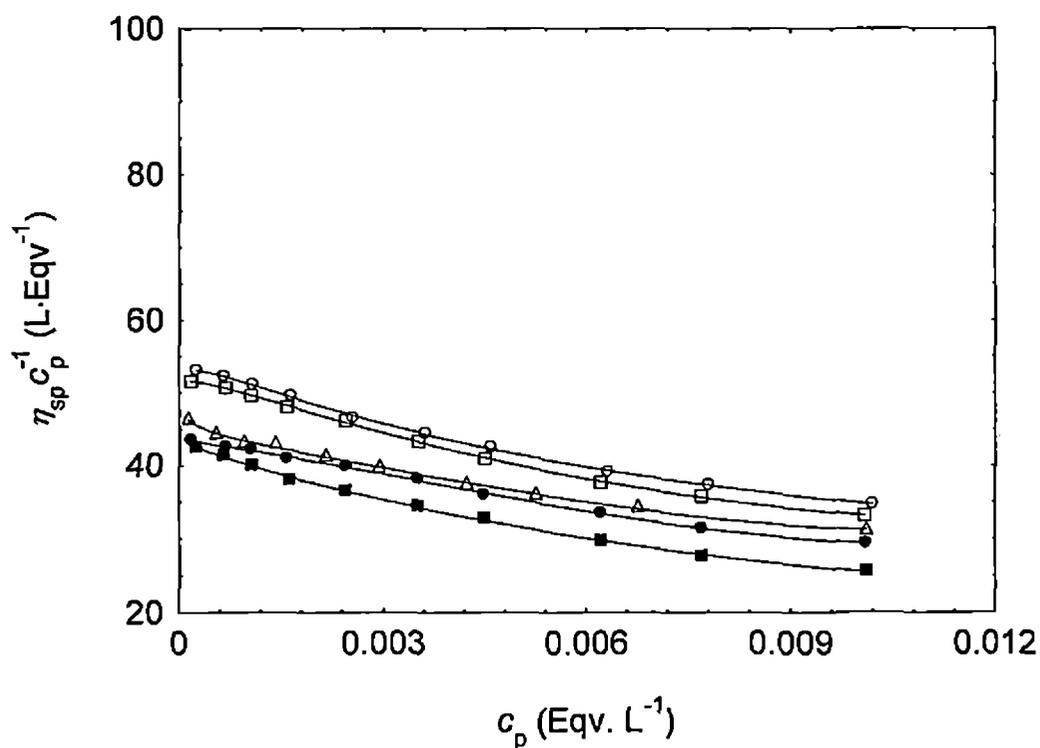


Figure 8.8 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 318.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass per cent; triangle: 25 mass per cent; closed circle: 40 mass per cent and closed square: 50 mass per cent). Lines are used to guide the eye.

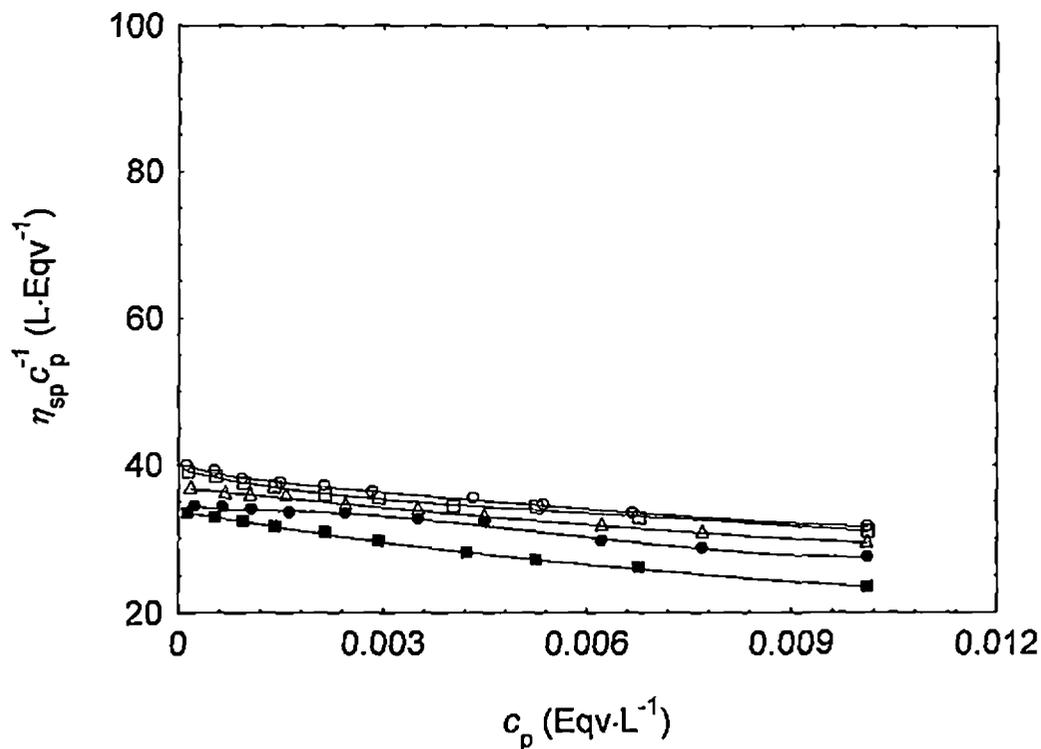


Figure 8.9 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 323.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass per cent; triangle: 25 mass per cent; closed circle: 40 mass per cent and closed square: 50 mass per cent). Lines are used to guide the eye.

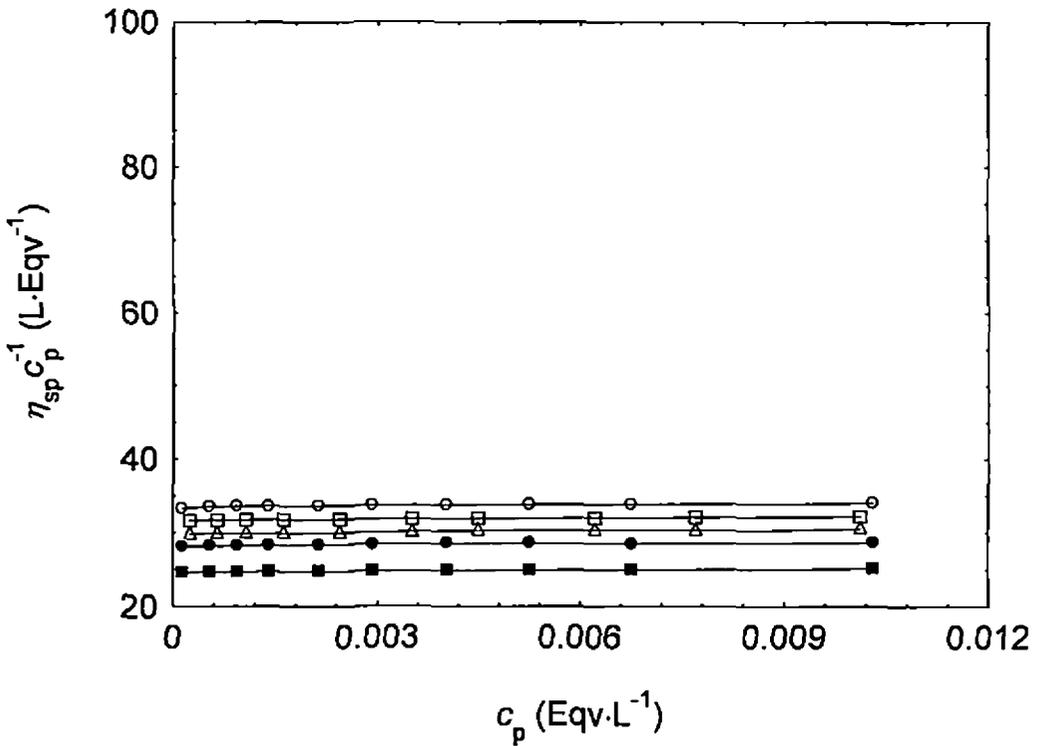


Figure 8.10 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 308.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol}\cdot\text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass percent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

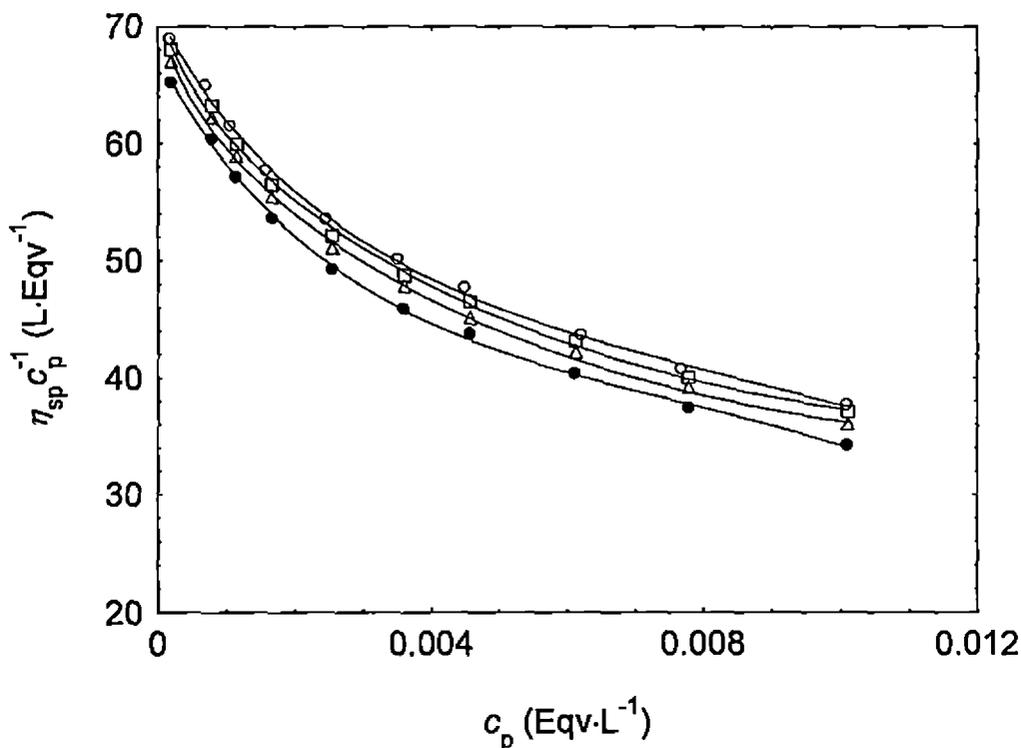


Figure 8.11 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in water in presence of the salt, NaCl, of concentration $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

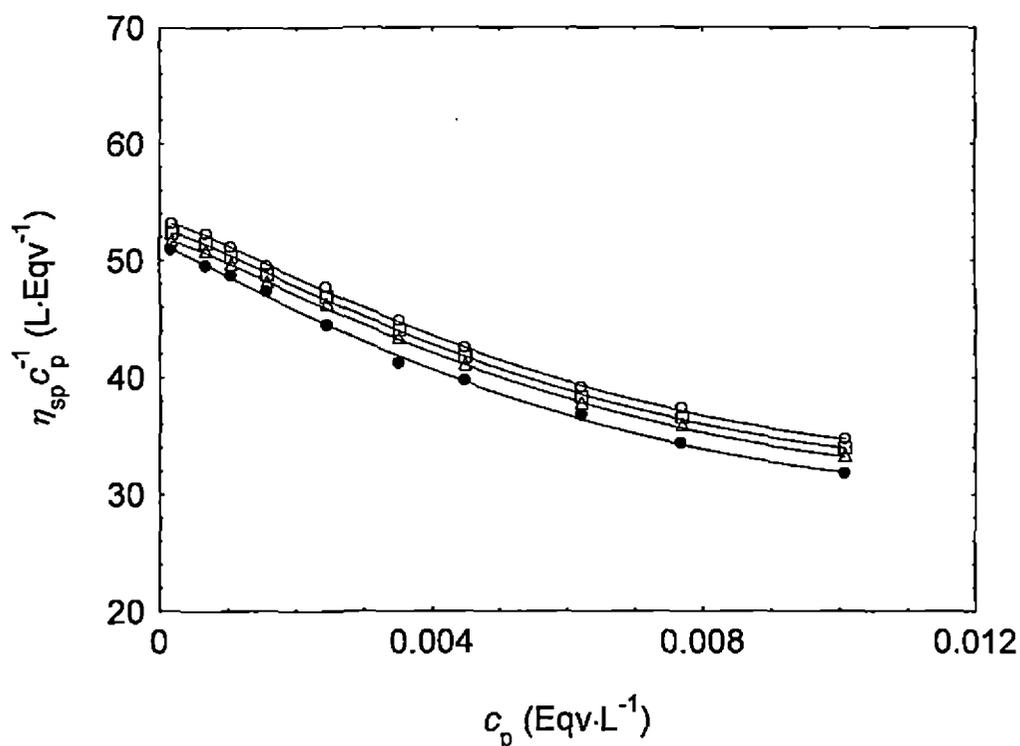


Figure 8.12 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 10 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of strength $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

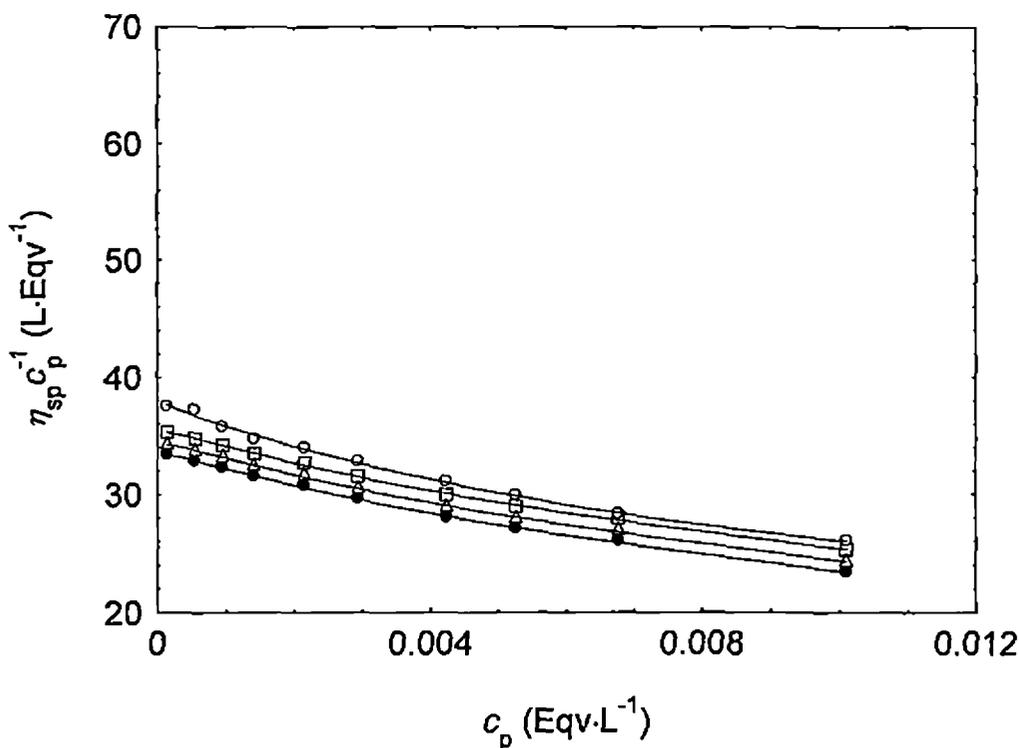


Figure 8.13 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 50 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

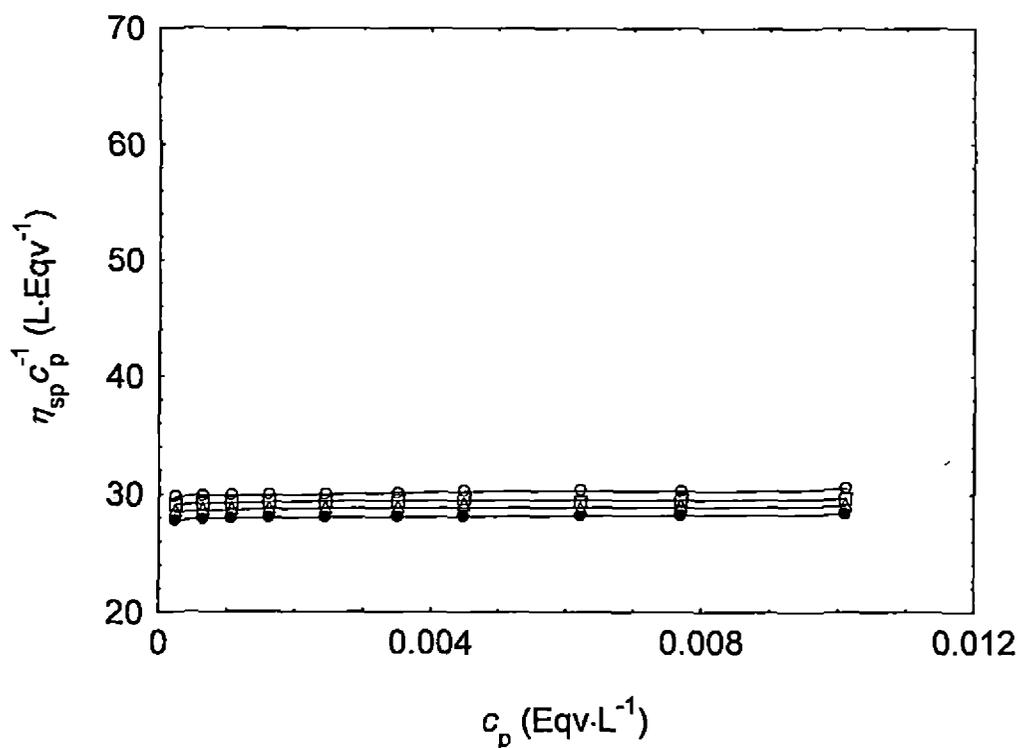


Figure 8.14 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 25 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$.

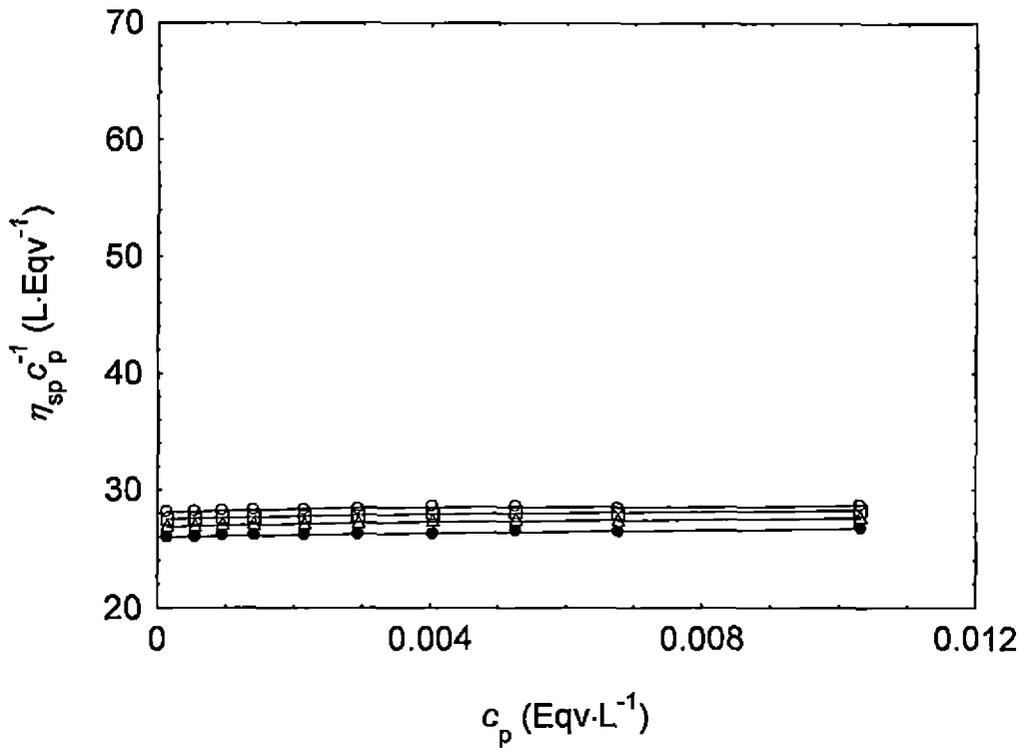


Figure 8.15 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp}/c_p) as a function of polyelectrolyte concentration (c_p) in 40 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$.

Chapter 9

Apparent Molar Volumes of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

9.1 Introduction

A detailed understanding of the solution behaviour of polyelectrolytes requires information on a variety of physical and chemical parameters. The partial molar volume is an important thermodynamic property which may be helpful in the identification of solute-solvent and solute-solute interactions. Moreover, partial molar volumes are necessary for the application of characterization methods and physicochemical techniques including analytical and preparative ultracentrifugation, as well as small – angle X-ray and neutron scattering. Empirical procedures have been developed to calculate and predict the limiting partial molar volume for nonionic and ionic organic compounds in aqueous solutions.^{1,2} However, the evaluation by these procedures for polyelectrolyte is limited due to lack of availability of reliable experimental data for a broad variety of chemical structures and macromolecular characteristics. A molecular theory of partial molar volume of polyelectrolytes which takes into account all types of interaction in these solutions is, so far, not available.

The principal factors that govern the dissolved state of polyelectrolytes in solutions are (i) the electro-repulsive forces working between ionic sites in the polymer chain and (ii) 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 corresponds to the 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 counterion condensation on the conductivity behaviour of sodium polystyrenesulphonate in

2-ethoxyethanol–water mixtures (*cf.* Chapters 6-8). We also have investigated the influences of intrachain and interchain electrostatic interactions and the resulting coiling/expansion of the polyion chains from viscosity measurements on the viscosity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures (*cf.* Chapters 9 and 10). In this chapter, we report the apparent molar volumes of sodium polystyrenesulfonate in 2-ethoxyethanol–water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

9.2 Experimental

2-Ethoxyethanol (G. R. E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $1.8277 \text{ mPa}\cdot\text{s}$ at 298.15 K ; these values agree well with the literature values.³ 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.

Sodium polystyrenesulphonate was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was 70000 and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 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.⁴ Measurements were made in a water bath maintained within $\pm 0.01 \text{ K}$ of the experimental temperature. The precision of the density measurements was always within $\pm 3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. Densities of 2-ethoxyethanol–water mixtures at 308.15 , 318.15 and 323.15 K are given in Table 9.1.

9.3 Results and Discussion

9.3.1 Apparent Molar Volumes

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

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

where c_p is the polyelectrolyte concentration (in monomolarity), M the molecular mass of the repeating unit of sodium polystyrenesulphonate with a degree of substitution (DS) of 1, ρ the density of the solution and ρ_0 the density of the solvent.

9.3.2 Variations of Apparent Molar Volumes with Polyelectrolyte Concentration

Figures 9.1 to 9.4 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixtures in 25, 40, 50 and 60 mass percent of 2-ethoxyethanol in 2-ethoxyethanol–water mixtures at 308.15, 318.15, and 323.15 K. Within the concentration ranges investigated here, the ϕ_v vs. $\sqrt{c_p}$ plots are found to be linear and, moreover, as $\sqrt{c_p}$ is increased, ϕ_v increased slightly. Similar linear increases for ϕ_v with concentration have been previously reported by Conway and Desnoyers,⁵ Lawrence and Conway,⁶ Ise and Okubo⁷ and Tondre and Zana⁸ for various polyelectrolytes in aqueous solutions although the insensitivity of ϕ_v toward concentration was also reported⁴ for salts of polystyrenesulphonic acid polyethylenimine. 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 2-ethoxyethanol–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 ϕ_v vs. $\sqrt{c_p}$ plots.

9.3.3 The Limiting Partial Molar Volumes

The apparent molar volumes at infinite dilution, ϕ_v^0 (equal to the limiting partial molar volumes, \bar{V}_2^0) were obtained by least-squares fitting of ϕ_v values to the equation

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

where S_v is the experimental slope. The values of ϕ_v^0 ($=\bar{V}_2^0$) are given Table 9.2. The correlation coefficients (r) of the regression analyses were always found to be greater than or equal to 0.990.

The limiting partial molar volumes are found to increase both (i) as the medium becomes richer in 2-ethoxyethanol at a given temperature, and (ii) as the temperature increases in a given mixed solvent medium.

9.3.4 Ionic Limiting Partial Molar Volumes

To investigate the specific behaviour of the polyion and the counterion comprising the polyelectrolyte, it is necessary to split the \bar{V}_2^0 values into their ionic components. Now in order to evaluate the limiting partial molar volume of polystyrenesulphonate ion, that of the sodium ion needs to be ascertained. As a representative case, we have executed the separation of the limiting partial molar volumes at 318.15 K. For this purpose, we have obtained the limiting partial molar volumes (\bar{V}_2^0) of sodium bromide (NaBr), sodium tetraphenylborate (NaBPh₄), and tetrabutylammonium bromide (Bu₄NBr) in 2-ethoxyethanol–water mixtures at 318.15 K from the measurement of their densities as a function of concentration. From these limiting partial molar volumes, the ionic limiting partial molar volumes of the sodium ion were obtained by the “reference electrolyte” method as suggested by Millero.⁹ We have used here tetrabutylammonium tetraphenylborate (Bu₄NBPh₄) as the reference electrolyte. The ionic limiting partial molar volumes of the sodium ion thus obtained were then subtracted from the limiting partial molar volumes of the polyelectrolyte as whole to obtain the respective contributions of the polyion. The ionic limiting partial molar volumes of the sodium and the polystyrenesulphonate ion in 2-ethoxyethanol–water mixtures at 318.15 K are listed in Table 9.3.

9.3.5 Various Contributing Factors to the Ionic Limiting Partial Molar Volumes

Following Millero,^{9,10} the ionic limiting partial molar volume, \bar{V}_{ion}^0 , can be attributed to the following components

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

where \bar{V}_{intr}^0 is the intrinsic partial molar volume (the positive increment in the \bar{V}_{ion}^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 volume¹⁰), \bar{V}_{elec}^0 is the electrostriction partial molar volume (the negative increment equal to the decrease in molar solute volume due to ion-solvent electrostrictive interaction), \bar{V}_{str}^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 \bar{V}_{cage}^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 sodium polystyrenesulphonate affect strongly the surrounding solvent molecules and hence for the polystyrenesulphonate polyion, \bar{V}_{elec}^0 will contribute significantly to its limiting partial molar volume. Because of the polar nature of 2-ethoxyethanol–water mixtures, the apolar part will also contribute to the polyion limiting partial molar volume through the term \bar{V}_{cage}^0 . Sodium ion, on the other hand, has nothing to do with caged partial molar volume.

9.3.6 Effect of Medium and Temperature on the Limiting Partial Molar Volumes

Table 9.3 shows that the limiting partial molar volume of the polyion increases initially with increasing amount of 2-ethoxyethanol in the 2-ethoxyethanol–water mixtures, reaches a maximum at around 50 mass percent of 2-ethoxyethanol and decreases thereafter. This indicates that the contribution of the term \bar{V}_{str}^0 overrides the sum of the contributions of the terms \bar{V}_{elec}^0 and \bar{V}_{cage}^0 below 50 mass percent of 2-ethoxyethanol in the mixed solvent media, whereas above 50 mass percent of 2-ethoxyethanol, the total contribution of the later two terms predominates over the contribution of the term \bar{V}_{str}^0 . The increment of the volume due to the destruction of solvent structure in the region of the ionic co-sphere is thus playing the major role in determining the limiting partial molar volume of the polyion when the mixed solvent media contain less than 50 mass percent of 2-ethoxyethanol. There is, however, a 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 beyond 50 mass

percent of the cosolvent in the medium. The influence of temperature on the limiting partial molar volume of sodium polystyrenesulphonate is very small. An increase in the temperature increases the limiting partial molar volume of sodium polystyrenesulphonate in a given mixed solvent medium as can be seen from Table 9.2. This might be ascribed to a slight growth 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 4).

9.4 Conclusions

The present investigation indicates that in 2-ethoxyethanol–water mixed solvent media counterion binding would become quite appreciable as the concentration of sodium polystyrenesulphonate is increased, thereby weakening the ion-solvent interactions. A delicate balance of the influences of the volumetric terms \bar{V}_{str}^0 , \bar{V}_{elec}^0 and \bar{V}_{cage}^0 is found to control the volumetric behaviour of this polyelectrolyte in 2-ethoxyethanol-water mixed solvent media. A temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures was also inferred from this study.

9.5 References

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Table 9.1 Densities (ρ_0) of 2-Ethoxyethanol–Water Mixed Solvent Media at 308.15, 318.15 and 323.15 K

T (K)	ρ_0 ($\text{g}\cdot\text{cm}^{-3}$)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
308.15	0.99758	0.99747	0.99361	0.98680
318.15	0.98807	0.98696	0.98004	0.96832
323.15	0.98394	0.98378	0.97610	0.96253

Table 9.2 Limiting Partial Molar Volumes (\bar{V}_2^0) of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solved Media at 308.15, 318.15 and 323.15 K

<i>T</i> (K)	\bar{V}_2^0 (cm ³ ·monomol ⁻¹)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
308.15	108.01 ± 0.02	109.03 ± 0.02	109.33 ± 0.01	110.65 ± 0.01
318.15	108.20 ± 0.01	109.11 ± 0.02	110.04 ± 0.02	110.84 ± 0.02
323.15	108.28 ± 0.03	109.22 ± 0.01	110.16 ± 0.02	110.93 ± 0.01

Table 9.3 Limiting Partial Molar Volumes, \bar{V}_{ion}^0 of Sodium Ion (Na^+) and Polystyrenesulphonate Polyion (PSS^-) in 2-Ethoxyethanol–Water Mixed Solved Media at 318.15 K

Ion / Polyion	\bar{V}_{ion}^0 ($\text{cm}^3 \cdot \text{monomol}^{-1}$)			
	Mass % of 2-Ethoxyethanol			
	25	40	50	60
Na^+	7.44	-0.60	0.14	2.27
PSS^-	100.76	109.71	109.90	108.57

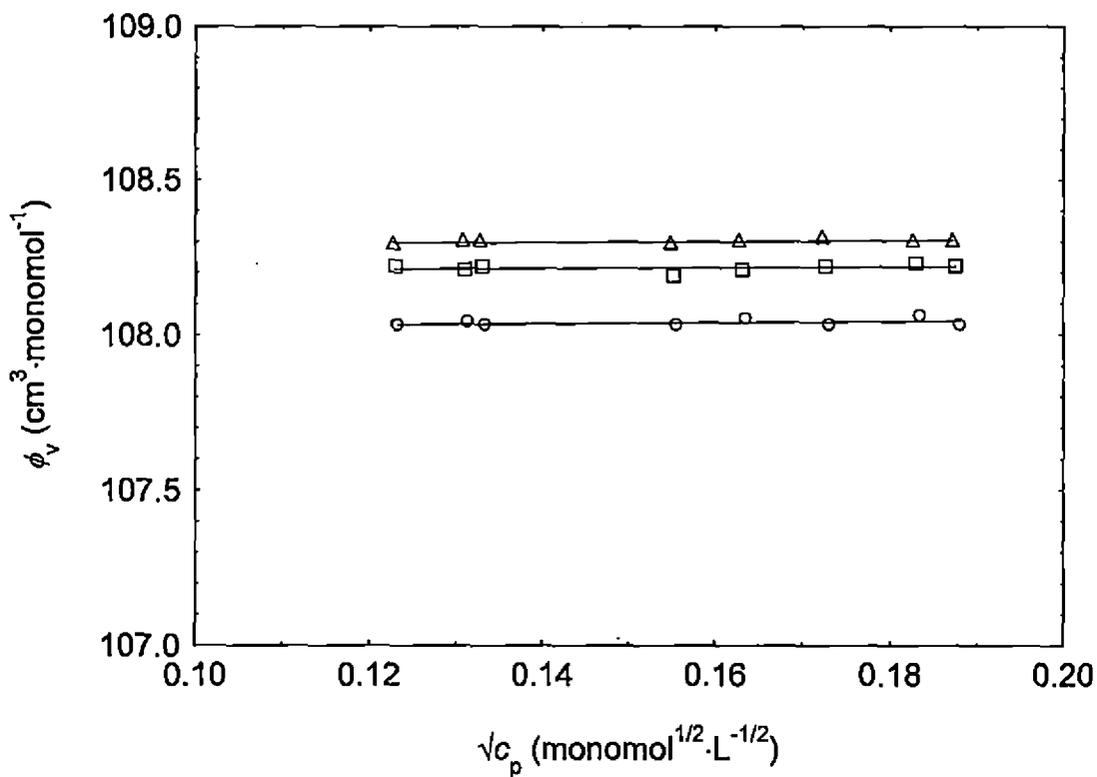


Figure 9.1 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (○); 318.15 K (◻); 323.15 K (Δ).

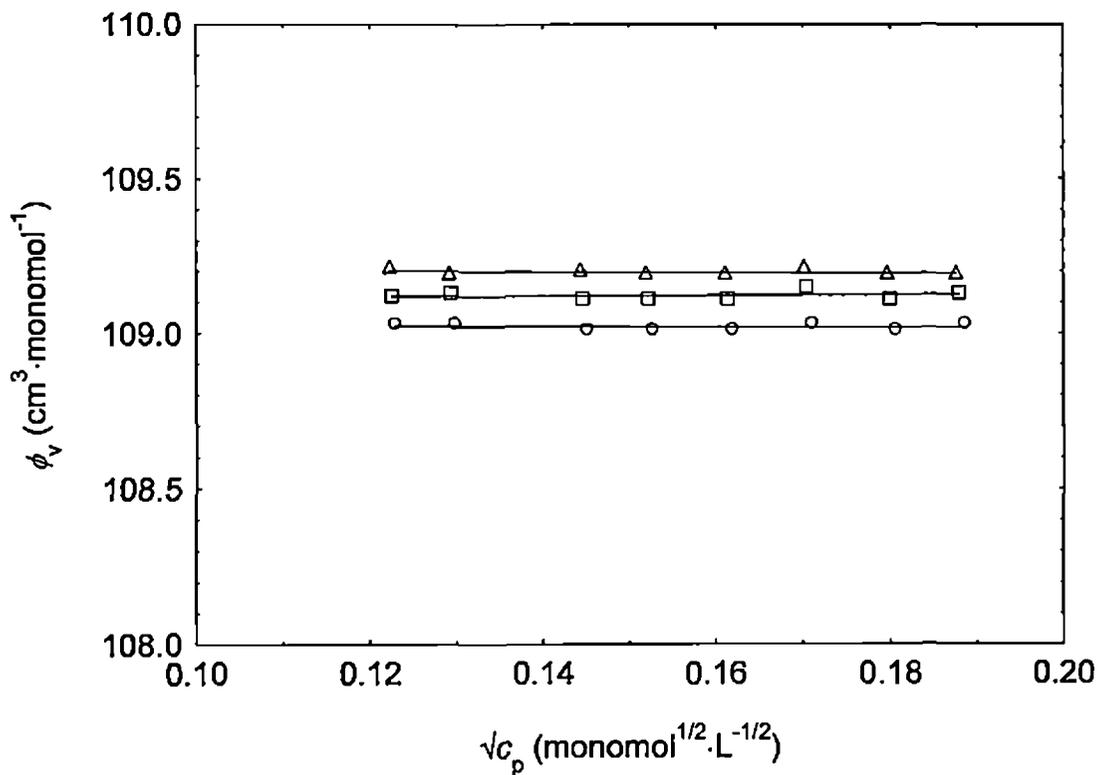


Figure 9.2 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (\circ); 318.15 K (\square); 323.15 K (Δ).

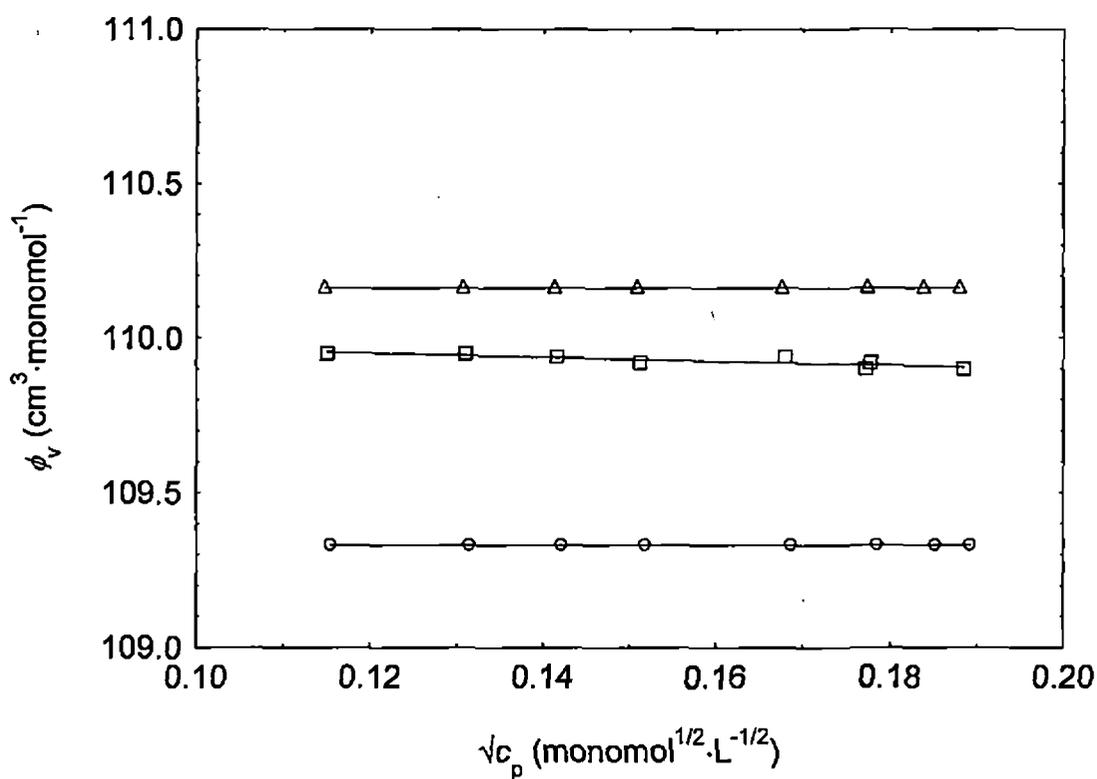


Figure 9.3 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 50 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (o); 318.15 K (□); 323.15 K (Δ).

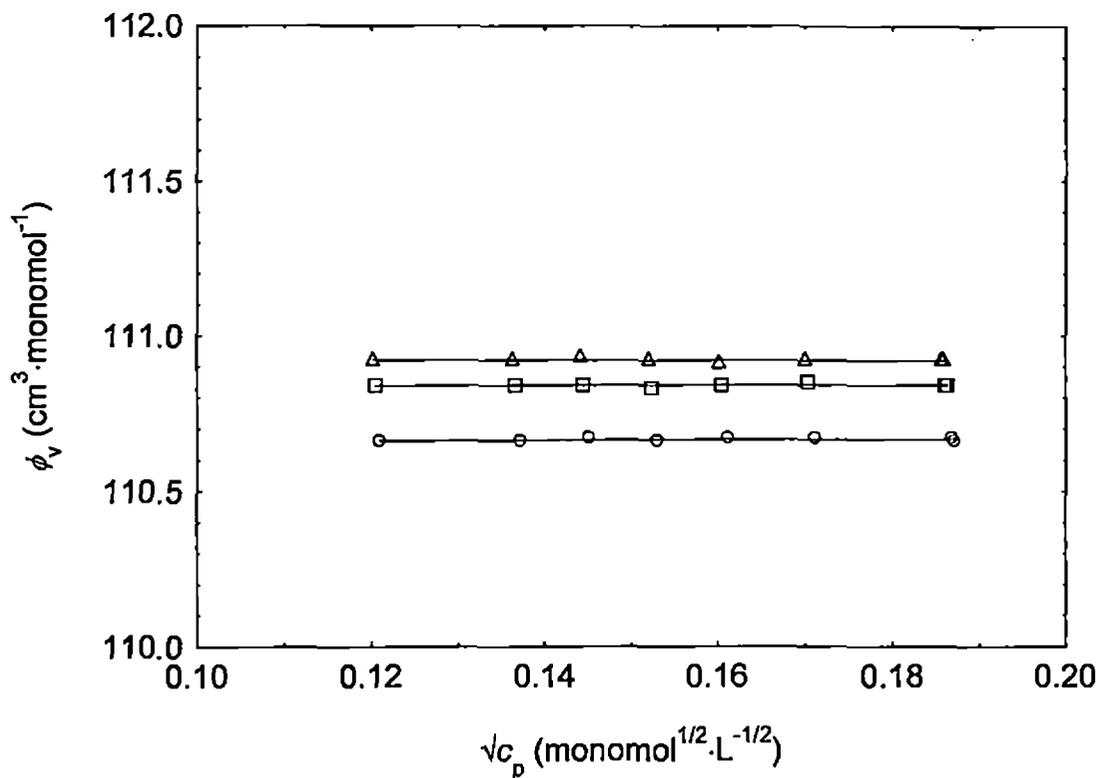


Figure 9.4 Polyelectrolyte concentration dependence of the apparent molar volumes of sodium polystyrenesulphonate in 60 mass percent 2-ethoxyethanol–water mixed solvent medium at 308.15 K (\circ); 318.15 K (\square); 323.15 K (Δ).

Chapter 10

Concluding Remarks

Polyelectrolytes exhibit numerous interesting properties that are now being actively investigated in many laboratories. Many important information and concepts on aqueous polyelectrolyte solutions have been derived from studies on their electrical conductivity, viscosity and density. However, very little attention has been paid to polyelectrolyte solutions in mixed solvent media despite the fact that the study of polyelectrolytes in these media is important in the sense that it 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 polystyrenesulphonate in 2-ethoxyethanol-water mixed solvent media using conductometry, viscometry and volumetry with a view to obtain precise information on the nature of interactions prevailing 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 polyion chain in semidilute solution offered a sharp improvement over the classical Manning counterion condensation model. There was, however, no suitable model for the description of the electrical conductivities of polyelectrolyte solutions in presence of salts when this project was taken up. During the course of this investigation, we have been successful in developing an equation following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a semidilute polyion chain according to Dobrynin *et al.* Excellent quantitative agreement between the experimental results and those using the equation developed was observed. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium polystyrenesulphonate in 2-ethoxyethanol-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 provided important insight into 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 volumetric studies.

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

Publications

List of Papers Published

1. Ion Association and Solvation Behaviour of Some 1-1 Electrolytes in 2-Ethoxyethanol Probed by a Conductometric Study, R. De, C. Guha and B. Das, *J. Solution Chem.*, **35**, 1505 (2006).
2. The Effects of Concentration, Relative Permittivity, and Temperature on the Transport Properties of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media, R. De and B. Das, *Eur. Polym. J.*, **43**, 3400 (2007).
3. Electrical Conductances of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media in the Presence of Sodium Chloride at (308.15, 313.15, 318.15 and 323.15) K, R. De and B. Das, *J. Chem. Eng. Data.*, **55**, 2108 (2010).
4. Conductivity, Transport, and Thermodynamic Investigations on the Counterion Condensation Behaviour of Sodium Polystyrenesulphonate in Ethylene Glycol–Water Mixed Solvent Media: Effects of Temperature, Medium and Polymer Concentration, C. Das, B. Das, and R. De *Polym. Intl.*, communicated.

