Solution Properties of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media

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Preface

Scope and Object of the Work

Polyelectrolytes are an important class of polymers which are both conductive and viscous. Since the emergence of polymer science, polyelectrolytes owing to their unique nature 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 as well as from their immense 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 pursued extensively. Complexes of polyelectrolytes with conjugated polymers *e.g.*, polyelectrolyte-polythiophenes and polyelectrolyte-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 in 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 although 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 in polyelectrolyte chemistry 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 more 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 the main subject of study.[7-10]

The principal factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces operative 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 to 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 neighbourhood of polyelectrolyte molecules. 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 carboxymethylcellulose) in methanol–water mixed solvent media using three different experimental techniques namely, electrical conductometry, viscometry and volumetry.

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Chapter 1

Summary of the Works Done

In this dissertation, we report the results of the studies on the solution behavior of a selected polyelectrolyte in mixed solvent media. Binary mixtures of methanol and water have been chosen as the solvent system in the present study. Sodium carboxymethylcellulose (NaCMC) has been chosen as the polyelectrolyte for investigation. Sodium carboxymethylcellulose - a semi-synthetic polyelectrolyte obtained by modifying a natural polysaccharide, cellulose, - is an important polyelectrolyte with a lot of industrial and applicational aspects.[1-7]

The present dissertation has been divided into nine 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 apparent 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 which have been used to obtain the results presented in the dissertation.

Chapter 4 reports the electrical conductivities of solutions of sodium carboxymethylcellulose in methanol-water mixed solvent media containing 10, 20 and 30 volume percent of methanol in absence of an added salt in the temperature range of 298.15 K – 328.15 K. The applicability of the Manning theory[8] for the electrical conductivity of salt-free polyelectrolyte solutions is examined and a major deviation from the theory was observed. Possible reasons for this deviation have been discussed. The effects of temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fractions of uncondensed counterions were also investigated. The applicability of the theory of semidilute polyelectrolyte conductivity proposed by Colby *et al.*[9] using the scaling theory approach to the experimental results of electrical conductivity of sodium carboxymethylcellulose in methanol-water mixtures was also tested. We have been able to quantitatively describe the electrical conductivity behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions. Variations of some of the thermodynamic parameters such as Gibbs free energy and association constants of counterion condensation on the polyion chain have been successfully determined.

In Chapter 5, the electrical conductivities of sodium carboxymethylcellulose in methanol–water mixed solvent media at 308.15 K in presence of sodium chloride, and sodium bromide have been reported. The conductance data have been analyzed on the basis of an equation developed by one of us 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.*[10] Excellent quantitative agreement between the experimental results and those using the equation developed was observed for both the salts.

In Chapter 6, the viscosity behaviour of sodium carboxymethylcellulose in water and in two methanol-water mixtures containing 10 and 20 volume percent of methanol at 308.15, using the isoionic dilution by using three electrolyte namely NaCl, KCl, and $BaCl_2$ has been investigated. The influences of the medium, total ionic strength, and charge on the intrinsic viscosities as well as on the Huggins constants have been interpreted from the points of view of the solvodynamic and thermodynamic interactions prevailing in the polyelectrolyte solution under investigation. Intramolecular and intermolecular contributions to the total viscosities have also been analyzed.

Chapter 7 describes the viscosities of sodium carboxymethylcellulose in aqueous and methanol-water mixed solvent media both in absence and in presence of NaCl with varying concentrations at 308.15 K. The results were analyzed in terms of a phenomenological approach for the viscosity of polymers solutions put forward by Wolf[11] in order to determine the intrinsic viscosities of the polyelectrolyte samples. This contribution presents a new and convenient method for the determination of the unperturbed and the perturbed root-mean-square radii of gyration of the polyion chains from the intrinsic viscosity values obtained in solutions with varying ionic strengths. The effect of solvent composition, molecular weight, and ionic strength on the viscosities and hence on the polyion coiling have been carefully examined.

Chapter 8 reports the apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent media within the temperature range 298.15-313.15 K. This investigation indicates that in methanol-water mixed solvent media counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Influences of the medium and the temperature on the limiting partial molar volumes have also been discussed.

The dissertation ends with some concluding remarks in Chapter 9.

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Chapter 2

Introduction

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

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

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

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

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

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

Polyelectrolytes

Definition of Polyelectrolytes

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

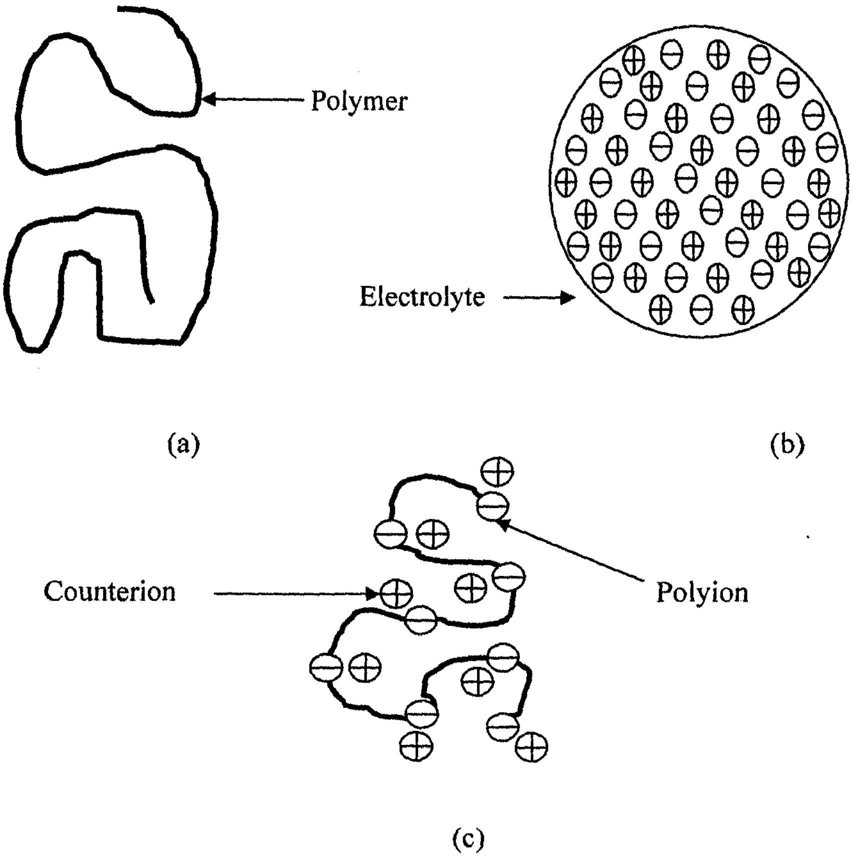
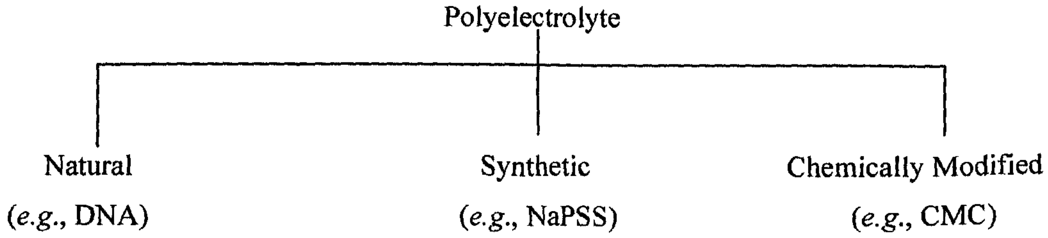


Fig. 1. (a) Polymer, (b) Electrolyte, and (c) Polyelectrolyte.

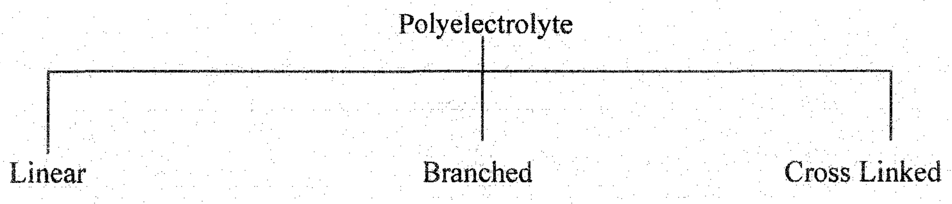
Classification of Polyelectrolytes

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



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

Depending upon their molecular architecture, polyelectrolytes have been divided into two important categories, namely linear and branched polyelectrolytes. In linear polyelectrolytes, a large number of atoms are connected together to form the backbone chain.



Although in a topological sense the backbone is linear, the shape of the polyelectrolyte might be quite different in solution. Due to their simple architecture they are used as model molecules in many investigations.[1] Branched polyelectrolytes do not have linear chains and are less investigated species compared to the linear ones.[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 (Figs. 1 and 2) comprises of a polyion which can undergo conformational changes and exhibit a complex behaviour resulting from intramolecular forces as well as strong intermolecular electrostatic interactions. Since both of these interactions occur almost simultaneously, it is rather difficult to study these systems. Sodium polystyrenesulfonate is an example of a flexible polyelectrolyte (Fig. 2). Rigid rod-like polyelectrolytes (Figs. 3 and 4) on the other hand, contains a polyion which does not undergo any conformational change due to steric constraints on such systems. Only the intermolecular Coulombic interactionsdetermine the solution properties of these polyelectrolytes. An example of this type of polyelectrolyte is poly (*p*-phenylene) with iodine counterions (Fig. 4). There are also examples of biologically occurring rigid rod-like polyelectrolytes such as DNA, ribonucleic acid (RNA) and the tobacco-mosaic virus.

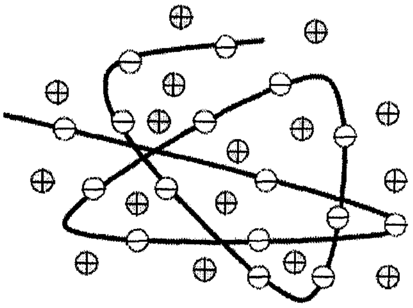


Fig. 2. Schematic representation of a flexible polyelectrolyte.

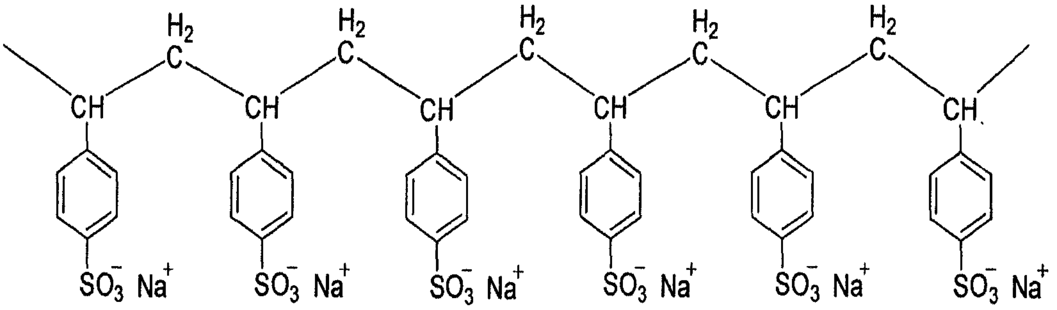


Fig. 3. An example of a flexible polyelectrolyte: sulphonated polystyrene with sodium counterions.

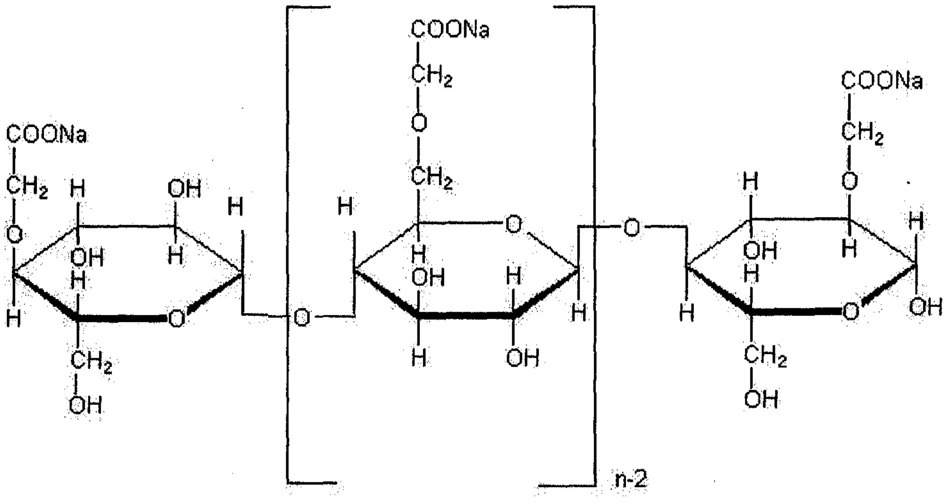


Fig. 4. Sodium carboxymethylcellulose with a degree of substitution of 1.

Importance of Polyelectrolytes

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

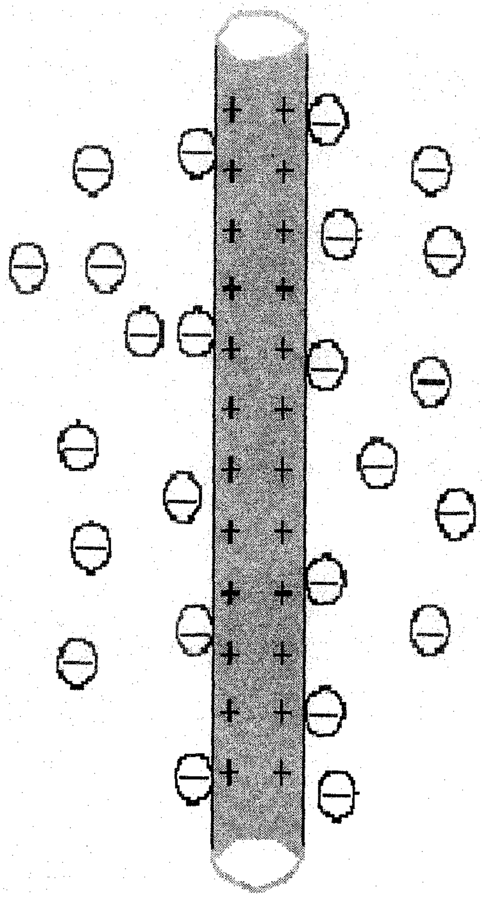


Fig. 5. Schematic representation of a stiff polyelectrolyte

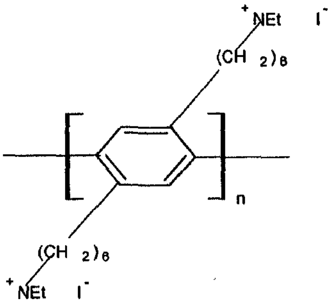


Fig. 6. A rigid rod-like polyelectrolyte: poly (*p*-phenylene) with iodine counterions.

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

Behaviour of Polyelectrolytes in Solutions

Concentration Regimes in Polyelectrolyte Solutions

The properties of polyelectrolytes in solution depend substantially upon their concentrations. There are three different concentration regimes in polyelectrolyte solutions. They are dilute, semidilute and concentrated regions. These could be understood from the concept of overlap concentration (c^*) defined as the concentration where the polymer chains start to overlap. A dilute polymer solution refers to the concentration region ($c < c^*$) where the polymer chains are well separted and do not interact with their neighbours. In such solutions, polyelectrolytes have a large overall size and a rather rigid local conformation.[14] The chain is represented by an extended rod-like configuration of N_D electrostatic blobs of diameter D in the dilute regime. Each of them, with g_e monomers, carries a charge of $q_D = z_c f e g_e$, where z_c is the counterion valence, e the electronic charge, and f the fraction of ionized charged groups on the polyion chain (*i.e.*, the fraction of uncondensed counterions). With the increase in the polyelectrolyte concentration, the polyion chains become more flexible. When $c < c*$, the chains begin to overlap and the conformations of the single chains are greatly modified. This region is known as the semidilute regime. The polyion chain is modelled as a random walk of N_ξ correlation blobs of diameter ξ_0, each containing g monomers in semidilute solutions. Each blob carries an electric charge of $q_\xi = z_c f e g$. Because of strong electrostatic interactions within each correlation blob, the chain is in a fully extended conformation of electrostatic blobs in the semidilute-unentangled regime ($c^* < c < c_e$). At higher concentrations where $c > c_e$, significant overlap of neighbouring chains occurs, and this strongly affects the chain motion (semidilute-entangled regime). The electrostatic blobs begin to overlap in much higher concentrations, and owing to the increase in electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments[15] suggest a polyelectrolyte behaviour similar to that of a neutral polymer solution.

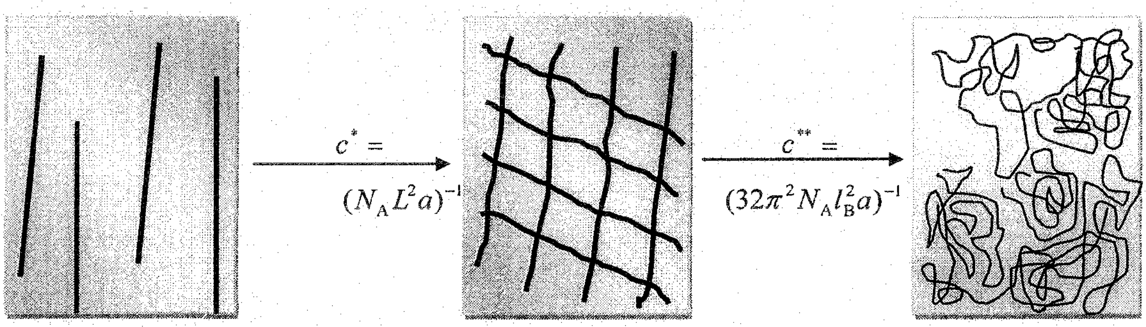


Fig. 7. Concentration regimes in polyelectrolyte solutions.

Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration, *i.e.*, a concentration c^*, at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the solvodynamic interactions are screened on length scales larger than the correlation length (*i.e.*, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the strand of N/g beads of size ξ_0). In short, a polyelectrolyte solution behaves as a concentrated solution for $c > c_D$, as an entangled-semidilute solution for $c_e < c < c_D$, as an unentangled-semidilute solution for $c^* < c < c_e$, and finally as a dilute solution for $c < c^*$. The available experimental evidences confirm the existence of more concentration regimes for polyelectrolyte solutions in the absence of added low-molar-mass salt than in its presence.[16] This evidence mostly stems from the study of nonequilibrium properties, such as viscosity, conductance, or diffusion. Experiments are difficult to perform below the overlap concentration because of the very low concentrations and subsequently very small effects to be monitored, requiring extreme experimental sensitivity. Measurements above c_D also might be problematic, arising from the high solution viscosity. It is, therefore, not surprising that most of the experimental results described in the literature seem limited to the concentration region between c_D and c^*. More extensive experimental investigations and further theoretical efforts are, therefore, required to arrive at the final conclusions as to the existence of these and other possible concentration regimes.

Brief Review of Some Important Investigations on Polyelectrolyte Solutions

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

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

Since the beginning of polyelectrolyte research, electrochemical methods have been employed as powerful tools to investigate and analyze the equilibrium properties and the transport phenomena[16,24,31,43] of polyelectrolytes. The availability of the sophisticated equipments in conjunction with the development of advanced theoretical approaches, contributed to the increasing significance of potentiometry and conductometry to explore the polyion-counterion interactions and to a better fundamental understanding of polyelectrolyte solution properties.

Solution behaviour of the polyelectrolytes have also been studied by various transport properties such as viscosity, sedimentation, diffusion, and electrophoresis.[16,19,24,25,31,43] Moreover, dielectric spectroscopy, osmometry and various scattering methods have been proven to be very useful in characterizing as well as in elucidating the behaviour of polyelectrolytes in solution.[2,31]

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

Viscosity is a property of the solution under the influence of a mechanical perturbation. On the other hand, diffusion phenomena are directly related to the relative motion of solute particles in a stationary system. Various kinds of isothermal diffusion may be distinguished, associated with different motions and are observed under different experimental conditions. For instance, the random motion of particles in a homogeneous system at thermodynamic equilibrium is responsible for density or concentration fluctuations. These motions are investigated by dynamic light scattering. Diffusional fluxes, on the other hand, arise in systems in which macroscopic chemical potential gradients exist for one or several thermodynamic species. An intermediate situation corresponds to the setup for self-diffusion measurement with fluxes of labelled molecules in a system containing a chemically identical species of different isotopic composition. All kinds of different diffusion measurements have been performed on polyelectrolyte solutions.[2] Diffusion of electroneutral components takes place in the presence of macroscopic concentration gradients. Diffusion is observed on the macroscopic scale where electroneutrality is observed locally. However, with the help of special experimental techniques, the motion of the separate charged species may eventually be followed and important information regarding the effect of ionic atmosphere on the macromolecular motion, changes in the average dimensions of the polyelectrolytes have already been derived.[2,16]

In principle, sedimentation measurements should provide information on the properties of salt-free polyelectrolyte solutions, but no appropriate theoretical approaches and experimental investigations are available at present, which allows the use of sedimentation measurements in this respect.[44] However, in presence of sufficiently high amounts of supporting low molar mass electrolytes, the motion of the polyions and the counterions is largely decoupled and ultracentrifugation is a powerful tool for molecular mass determination. Additionally, the conformational changes of the polyions with varying salt concentration can be studied, because the sedimentation velocity is proportional to the reciprocal of the frictional coefficient. Comprehensive reviews of sedimentation analysis of polyelectrolyte solutions are available in Budd.[2,45,46]

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

All of the commonly measured colligative properties of simple ionic solutions *e.g.*, Donnan equilibrium, osmotic pressure etc. are also capable of characterizing polyelectrolyte solutions.[2] These properties have been extensively employed to a great variety of natural and synthetic polyelectrolytes to investigate the polyion-counterion interactions and to estimate the fractions of uncondensed counterions. In the literature,[2,16,51-56] substantial amount of information on the osmotic coefficients and the Donnan equilibria of polyelectrolytes is available. Moreover, several investigations on the osmotic coefficients of a synthetic rod-like (rigid) polyelectrolyte solutions have also been performed to test various models of polyelectrolyte solutions describing the electrostatic interactions of the counterions with the polyion[55,56] and the results clearly demonstrated the failure of the Manning and the Poisson-Boltzmann cell models. Afterwards, an analysis performed by Deserno *et al.*[57] on the osmotic coefficients of two rod-like polyelectrolytes namely, DNA and poly(*p*-phenylene) using molecular dynamics (MD) simulations and the Debye-Hückel-Hole-Cavity (DHHC) theory and concluded that they indeed give a good description of the influence of the correlations of the counterions with the polyion.

The dielectric properties of aqueous solutions of polyelectrolytes present a very complex phenomenology, not yet understood completely. The century-old dielectric methods are still one of the most important techniques for studies on the structure and dynamics of polymer solutions. This is due to the capability of these methods to investigate the relaxation processes occurring in aqueous polyelectrolyte solutions in an extremely wide range of characteristic times, approximately from 10^{-12} through 10^{3} s. Information on the effective charge on the polyelectrolyte chains, the fraction of condensed counterions, and the effective friction coefficient of condensed counterions, can be obtained from dielectric spectroscopic techniques.[31]

Static light scattering (SLS), small-angle X-ray scattering (SAXS), and small angle neutron scattering (SANS) are classical scattering methods, and are of special importance in the characterization of the molecular parameters of polyelectrolytes in solution.[32,58-61] There has been an increasing interest in dynamic scattering methods, particularly dynamic light scattering (DLS) for the past four decades, because these could provide important insight into the dynamics of polyelectrolyte solutions to very high concentration, and these are also capable of providing useful structural informations, *e.g.*, translational diffusion coefficient and solvodynamic radius of the scattering species.

The main focus of light scattering studies on polyelectrolyte solutions was, up to about 1980, on the coil expansion and the second virial coefficient as a function of the ionic strength of the medium, besides their role in routine determination of the mass average molecular mass.[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 or in very dilute salt solutions. Compared to the static light scattering experiments, small-angle X-ray scattering studies lead to structural information about small distances (2-100 nm). The main field is the investigation of the structural details of chain conformation.[64,67,68] For the characterization of biopolymers, such as proteins and nucleic acids, SAXS plays a very important role. Besides the determination of molecular mass, information on the dimension, geometric form, and internal structure of the biopolymers is available from SAXS studies.[69-72] For unfolded proteins, the chain statistics may be checked by SAXS in conjunction with, for instance, SLS and DLS, which provides the opportunity to determine several independent parameters such as molecular mass, radius of gyration, hydrodynamic radius, persistence length, and virial coefficient.[73,74]

Conventional SANS experiments provide information on the mass and the radius of gyration of the aggregated clusters; the labelling technique allows the single chain conformation of the polyelectrolyte molecules incorporated into the clusters to be determined.[75-82]

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 concentration, ionic strength, and molecular mass.[2,83-85]

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

Even if considerable attention has so far been paid to the studies of polyelectrolyte solutions using various available experimental techniques described above, there is very little work in the literature dealing with the effect of the medium in mixed solvent systems, and the temperature on the interactions between a polyion and its counterions[86-93] 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 polyelectrolyte behaviour from a more general point of view. Studies in such systems, hence, could provide important insight into the fundamental understanding of the interactions between the polyions and the counterions and also on the conformation of the polyions in solution.

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

Some Important Properties of Polyelectrolyte Solutions

Polyelectrolyte Conductance

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

Salt-Free Polyelectrolyte Solutions: The Manning Counterion Condensation Model

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

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by[19,94-98]

$$\xi = \frac{e^2}{bDk_\mathrm{B}T} \qquad (1)$$

where e is the protonic charge, D the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzmann constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, sufficient number of counterions condense onto the polyion to give the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law for the equivalent conductivity of a salt-free polyelectrolyte solution is related to ξ by the following equation[95,96]

$$\Lambda = f(\lambda_c^0 + \lambda_\mathrm{p}) \qquad (2)$$

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

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

Contrary to Huizenga[99] where the counterions are regarded either as "bound" or as "free" implying that they are not influenced by the polyion, Manning assumed that the condensed counterions, certainly can be considered as bound, the fraction of such ions being

$1-\xi^{-1} \neq 1-f$, while the uncondensed counterions may, in no way, be thought of as free, being subjected to the Debye-Hückel potential of the polyions. Thus f does not have the significance of the fraction of free counterions rather it represents the fraction of uncondensed counterions. Considering the contributions due to electrophoretic and relaxation effects to the equivalent conductivity, the polyion equivalent conductivity λ_p was derived theoretically for the cylinder model of polyelectrolytes,[97] and for counterions with a charge of z_c it can be expressed as

$$\lambda_\mathrm{p} = \frac{279A|z_\mathrm{c}|^{-1}|\ln \kappa a|}{1+43.2A(|z_\mathrm{c}|\lambda_\mathrm{c}^0)^{-1}|\ln \kappa a|} \tag{4}$$

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

$$A = \frac{Dk_\mathrm{B}T}{3\pi\eta_0 e} \tag{5}$$

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

$$\kappa^2 = \frac{4\pi e^2}{\mathrm{D}k_\mathrm{B}T}\xi^{-1}n_\mathrm{e}|z_\mathrm{c}| \tag{6}$$

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

Limitation of the Manning Model

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

Previous studies indicated that although within a limited concentration range, the concentration dependence of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not, in general, agree with the predictions. This aspect has been amply described in the reviews by Bordi *et al.*[31] and Wandrey and Hunkeler[43] and no attempt is, therefore, made here to provide a detailed review of the vast literature that exists on this subject. However, some of the important results will be discussed here. The article in which Manning presented[96] the complete theoretical equation for the equivalent conductance of a salt-free polyelectrolyte solution in the limit of zero polyelectrolyte concentration was published in 1975. Quite interestingly, the two subsequent articles by Kwak and Hayes[100] 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 Hayes[100] studied the electrical conductances of lithium, sodium, potassium, cesium, magnesium, calcium, and strontium salts of polystyrenesulfonic acid covering the dilute and semidilute regimes (*i.e.*, above and below the overlap concentration, c^*) at 298.15 K. They observed a minimum in the equivalent conductivity in the range 7×10^{-3} to 1×10^{-2} monomol.L^{-1} for all counterions and for the two investigated polyelectrolytes with molar masses of 70,000 and 500,000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the subsequent increase beyond the minimum could not be accounted for. It was concluded that the applicability of the Manning theory is questionable for a concentration range where the polyion chain tends to coil. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonic acid in semidilute solutions were carried out by Szymczak *et al.* at 298.15 K.[101] Positive deviations from the limiting law are evident even at the lowest concentrations investigated. They suggested that the Manning theory for electrical transport properties might require additional theoretical considerations.

Other studies by Kwak *et al.*[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 with different charge density parameters that, although qualitative agreement is obtained with the Manning limiting law, the concentration dependence predicted is in agreement with the experimental curves only for the polyions with a relatively low charge density. The conductivity behaviour of dextran sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rodlike structure on which the theory is based.

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

The concentration dependence of the equivalent conductivity of aqueous tetra-*n*-alkylammonium salts of pectic acid above and below the overlap concentration also manifested large deviation from the Manning limiting law.[92]

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

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

The study by Rios[106] on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-*co*-(vinyl pyrrolidone)], Rios[106] paid the attention below the overlap concentration. Whereas the Manning model predicts a slow but monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration, a maximum was experimentally observed in each of these three cases. The agreement between the experiment and theory is generally poor; the theoretical curves are, however, found to approach the experimental ones for the lithium and sodium salts over a very narrow concentration range in very dilute solutions.

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

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

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

A successful model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*[112] using the scaling description proposed by Dobrynin *et al.*[113] for the configuration of a polyion chain. In the semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of diameter ξ_0, each of them containing g monomers. Each blob bears an electric charge of $q_\xi = zefg$ (z being the counterion valence, e the electronic charge and f the fraction of uncondensed counterions) and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge of $Q_\mathrm{p} = N_\xi q_\xi = zefgN_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of diameter 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 diameter 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 diameter ξ_0. Within this model, in absence of an added electrolyte, the equivalent conduvtivity can be calculed by an equation.

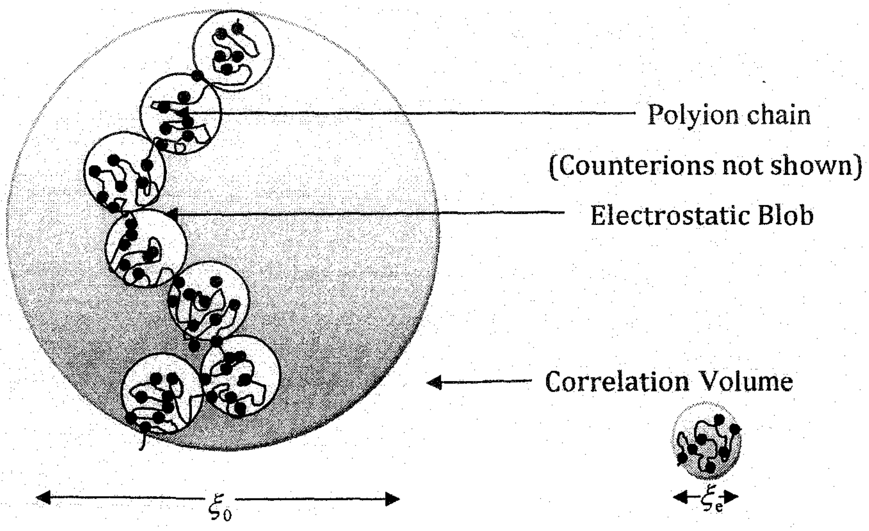


Fig. 8. Schematic diagram of correlation volume in a semidilute polyelectrolyte solution.

The equivalent conductivity of a polyion in a semidilute solution is given by

$$\lambda_{\mathrm{p}} = \frac{Fzefg \ln(g/g_e)}{3\pi\eta_0\xi_0} \tag{7}$$

where F is the Faraday constant and η_0 is the coefficient of viscosity of the medium.

Under the condition of $g/g_{\mathrm{e}} = \xi_0/\xi_{\mathrm{e}}$ and making use of the fact that the electrostatic blobs are space filling ($g = c\xi_0^3$, c being the monomer number density) Eq. (4) reduces to

$$\lambda_{\mathrm{p}} = \frac{Fzefc\xi_0^2 \ln(\xi_0/\xi_e)}{3\pi\eta_0} \tag{8}$$

The equivalent conductance of the polyelectrolyte solution is then given by

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

The above expression was derived by Colby *et al.*[112] taking into account the scaling arguments proposed by Dobrynin *et al.*[113] neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. It may be seen from Eq. (9) that the above model relies on a single free parameter *f*, the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polyelectrolyte concentration given by the value of the charge density parameter $\xi = \lambda_{\mathrm{B}}/b$, Eq. (9), can be applied to more concentrated systems, up a concentration of c_{D}, where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size.

This model has been applied, so far, to a limited number of aqueous polyelectrolyte systems[31,93,112,114] and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify the concentration regimes differing in the fractions of uncondensed counterions.[115] This model, however, has not been applied to polyelectrolyte solutions in solvents besides water with the exception of an attempt by one of us for sodium polystyrenesulfonate and sodium carboxymethylcellulose in methanol-water mixed solvent media.[110, 111]

Effect of Salts on the Conductance of Polyelectrolyte Solutions

Although the polyelectrolyte conductivities have been well understood in salt-free semidilute solutions[112.114] in the light of the scaling description for the configuration of a polyion chain in accordance with Dobrynin *et al.*,[113] the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions. Devore and Manning[116] were the first to make an attempt to describe the electric transport properties of polyelectrolyte solutions in presence of a simple salt using the Manning counterion condensation theory[95] 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.[117-121]

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 by adding the value of specific conductance of salt and polyelectrolyte.The equation is

$$\kappa = \kappa_{\mathrm{p}} + \kappa_{\mathrm{S}} \tag{10}$$

where κ_{p} is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_{s} is the specific conductance of the simple salt in the absence of polyelectrolyte.

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

Later Kowblansky and Ander[117] modified the "primitive" additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa = \kappa_p + \kappa_S \left(D_2 / D_2^0 \right) \tag{11}$$

where D_2 and D_2^0 are the coion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2 / D_2^0 has been used as a quantitative measure[95] of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s \left(D_2 / D_2^0 \right)$.

Although the "modified" additivity has been shown to be somewhat superior to the "primitive" one, the departures from the experimental results are not yet accounted for.[117-121] Later, Bordi *et al.*[122] evaluated the equivalent conductances for a hydrophilic polyion with a salt in the light of scaling theory approach[113] and compared them with their experimental results. The agreement is rather good, although a quantitative description is still awaited.

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

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

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

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

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

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

The total specific conductivity of a polyelectrolyte solution with added simple electrolyte should, thus, be equal to the sum of the specific conductivity of the simple salt in the absence of a polyelectrolyte and the effective specific conductivity due to the polyelectrolyte in the presence of the simple salt

$$\kappa = \kappa_{\mathrm{S}} + f'c\left[\lambda_c^0 + \frac{c\,\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{14}$$

In the above equation, f' has been treated as an adjustable parameter and this can be conveniently obtained by the method of a least-squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in presence of a salt to Eq. (14) provided κ_s is known. This value of f' takes care of the changed polyion-counterion interactions under the influence of the added salt. The second term in Eq. (14) is the actual contribution of the polyelectrolyte species towards the total specific conductivity in the presence of an added salt.

Polyelectrolyte Viscosity

Viscosity of Polyelectrolytes as a function of Concentration

Viscosity is an important tool for the determination of molecular structure and conformation of both neutral and charged polymers. Polyelectrolyte solution viscosity depends very much not only on the chemical structure of the polyion, its size and charge density, but also on the environmental properties such as the ionic strength and the solvent polarity.[125-136] In case of neutral polymer solutions, the reduced viscosity η_{sp}/c (defined as $\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$, where η is the viscosity of the solution, η_0 is the viscosity of the solvent alone and c is the (monomer) concentration of the polyelectrolyte solution) is proportional to c. This well-known relation (known as the Huggins equation[2]) is used for determining the intrinsic viscosity $[\eta]$ simply by extrapolation of η_{sp}/c values to $c = 0$. On the other hand, salt-free polyelectrolyte solutions exhibit an anomalous dependence of viscosity on concentration. Early investigations on the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that reduced viscosity would increase monotonically as the polyion concentration is reduced. In these studies, which are summarized in the pioneering work of Fuoss,[125,126] a straight line is obtained when inverse reduced viscosity is plotted as a function of the square root of the polymer concentration. It is usually assumed that this straight line could be extrapolated to zero concentration and that the intercept at zero polyelectrolyte concentration gives the reciprocal of the intrinsic viscosity. However, careful investigation of the dilute solution behaviour revealed that the apparently unbounded increase of the reduced viscosity is always followed by a maximum,[127-130] and normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. It has been argued that the observed behaviour is a consequence of screening of long-range intermolecular interactions by the residual electrolyte in the solution, an explanation supported by the observation of "regular" neutral polymer behaviour upon isoionic dilution of polyelectrolyte solutions.[130] The anomalous shape of the curve of the reduced viscosity versus concentration for dilute salt-free solutions, found in many studies, was generally interpreted as the result of expansion and contraction of the flexible polyion due to short-range interactions. Most of these investigations were performed on weak polyelectrolytes *e.g.*, derivatives of polyvinylpyridine and polymers containing carboxylic acids, as reviewed by Tanford.[131] Hodgson and Amis[132,133] 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,[134,135] poly (galacturonic acid) sodium salt,[136] sodium polystyrenesulfonate,[128,137] sodium carboxymethylcellulose,[138] polysulfobetaines,[139-142] and polyelectrolytes with poly(*p*-phenylene) backbone[143] etc.

In 1987 Witten and Pincus put forward a theory for the viscosity of polyelectrolyte solutions which was derived for solutions near the overlap concentration.[144] Later Cohen *et al.*[128,129] derived a similar relation on the basis of the theory by Hess and Klein[145] and have shown that the relation derived fits well the experimental results with some adjustable parameters. Both of these approaches are characterized by assumptions that viscosity is dominated by intermolecular interactions which are primarily electrostatic in nature and by the treatment of the solution as a simple viscoelastic liquid. However, despite the success of these treatments to a limited number of systems, the assumptions underlying these approaches are questionable. Another interesting approach to the viscosity problem has been presented by Nishida *et al.*[146] who calculated the viscosity of interacting spheres (point particles) according to an old theory of Rice and Kirkwood.[147] The interaction between the particles is described by a Debye-Hückel potential which exhibits a maximum as a function of polyion concentration. The maximum in the interaction energy is manifested by the maximum of the viscosity. The calculation may be employed to separate formally the influence of interaction and of conformational change of the polyion on the experimental viscosity data.

In their approach Nishida *et al.*[146] 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.*[148] demonstrated that the maximum in the viscosity curve can be described by using the Hess and Klein approach.[145] On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of a salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following equation,

$$\eta_{sp}/c \sim c/\kappa^3 \tag{15}$$

where c, the polyelectrolyte concentration is expressed in Eqv.L^{-1} and κ is the inverse Debye screening length.

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

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

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

when ξ is >1 or ≤1, respectively.

Antonietti *et al.*[148,149] expressed the reduced viscosity for charged latex particles as:

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

in which $(\eta_{sp}/c)_{HK}$ represents the electrostatic contribution expressed in Eq. (15). Besides describing the polyelectrolyte concentration dependence of the reduced viscosity, Eq. (18), in principle, is capable of recovering the intrinsic viscosity of the polyelectrolyte solution. Antonietti *et al.*[148] observed that although a quantitative fit according to Eq. (18) could describe the polyelectrolyte behaviour in acetone, isopropyl alcohol, and ethanol, it was impossible to extract qualitative information, since each parameter value is rather unstable.

Intrinsic Viscosity

In discussing the conformation of single polymer chain from viscometric data, information about the intrinsic viscosity $[\eta]$ is indispensable. Moreover, this parameter also plays an important role in the molecular mass determination of polymer. For salt-free and low salt-containing polyelectrolyte solutions, however, the determination of this parameter presents a great challenge due to the anomalous concentration dependence of viscosity of polyelectrolyte solutions in these cases.

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

At a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity η_{sp}/c varies linearly with the polymer concentration (c) similar to that for a neutral macromolecular solution, provided there is an excess of low molar mass electrolyte thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation[2,150]

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

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

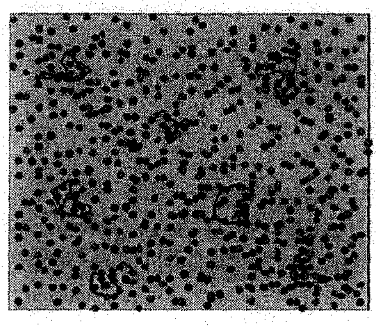


Fig. 9. Elimination of polyelectrolyte effect by addition of a large excess of a salt.

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

The intrinsic viscosities can be determined in a more straightforward manner using the method of isoionic dilution.[130,151] Following this method, a polyelectrolyte solution in the pure solvent (in absence of any low molar mass salt) is diluted with solutions of increasing concentration of a salt. The dilution of the solution is performed in such a manner that after each addition, the total ionic strength of the solution remains the same and equal to the initial value due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these conditions the reduced viscosity exhibits a linear decrease as one lowers the polyelectrolyte concentration and hence extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength. Moreover, since the ionic environment around the polyions remains unaffected as a result of isoionic dilution, the original conformation of the polyion under salt-free situation is assumed to be preserved.

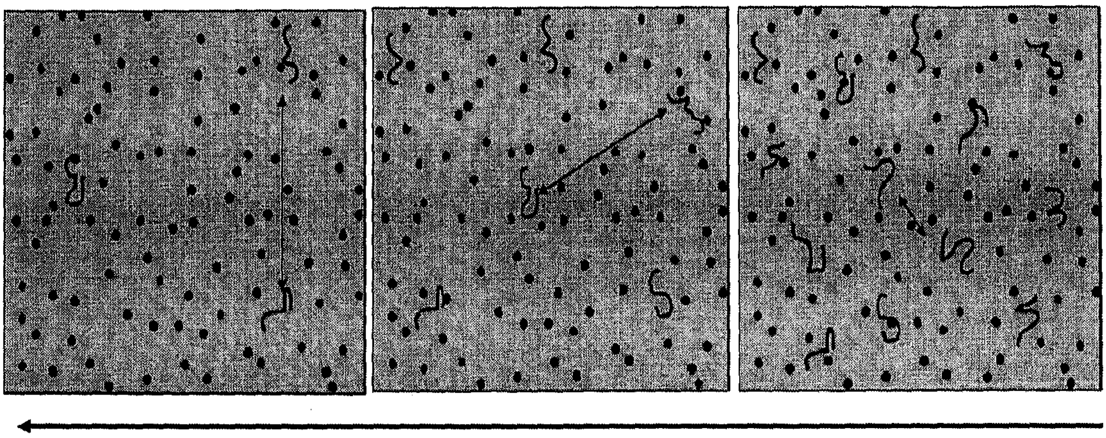


Fig. 10. Schematic representation of isoionic dilution.

In spite of the success of this isoionic dilution method for the determination of intrinsic viscosity in a convenient manner, however, very little attention has been paid to this direction so far.[130,135,151-154]

***Determination of Intrinsic Viscosity of a Polyelectrolyte by Wolf Method*[155]**

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

As long as the viscosity η of the solutions constitutes a variable of state, the intrinsic viscosity $[\eta]$ is given by the initial slope of the dependence of the natural logarithm of the relative viscosity $\ln\eta_{\mathrm{rel}}$ (η_{rel}= viscosity of the solution/viscosity of the solvent) on polymer concentration c (mass/volume). Under these conditions one can write

$$\mathrm{d}\ln\eta = \left(\frac{\partial\ln\eta}{\partial c}\right)_{T,\mathrm{p},\gamma}\mathrm{d}c + \left(\frac{\partial\ln\eta}{\partial c}\right)_{\mathrm{c,p},\gamma}\mathrm{d}T + \left(\frac{\partial\ln\eta}{\partial c}\right)_{\mathrm{c},T,\mathrm{p}}\mathrm{d}\gamma \qquad (20)$$

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

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

The intrinsic viscosity itself can then be defined as

$$\lim_{c\to0,\gamma\to0}\left(\frac{\partial\ln\eta}{\partial c}\right)_{\mathrm{T,p},\gamma} = \lim_{c\to0,\gamma\to0}\{\eta\} = [\eta] \qquad (22)$$

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

Partial Molar Volumes of Polyelectrolytes

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

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

where m is the polyelectrolyte concentration (in moles of monomer per kg of solvent), M the molecular mass of the monomeric unit of the polyelectrolyte under study, ρ the density of the solution and ρ_0 the density of the solvent.

In majority of the polyelectrolyte solutions investigated, the partial molar volumes were found to remain practically constant over the concentration ranges investigated though it is true that they vary slightly with concentration for a few cases.[159-164] In the former cases, the partial molar volumes at infinite dilutions (ϕ_v^0) have usually been considered as the mean of the observed ϕ_v values, whereas in the later cases these were determined by extrapolating ϕ_v values to zero concentration of the polyelectrolyte. 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.[165,166]

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 electrostrctional hydration effect, the hydrophobic structural effect, and counterion-binding onto the polyion chain in polyelectrolyte solutions were interpreted on the basis of this property.[159-162,167-169] Empirical procedures have been developed to calculate and predict the partial molar volumes for non-ionic and ionic organic compounds in aqueous solutions.[170,171] However, the evaluation of the partial molar volumes by these procedures has not been attempted in mixed solvent media because of the lack of availability of reliable experimental molar volume data for a broad variety of polyelectrolyte in such solvents.

Present Investigation

From the above discussion, it is apparent that the problem of polyion-polyion and polyion-counterion interactions is challenging as well as interesting. It is, therefore; desirable to explore this aspect using different experimental techniques to arrive at a definite conclusion. Moreover, investigations in mixed solvent media provide the opportunity to study the behaviour of polyelectrolyte solutions from a more general point of view compared to those in aqueous solutions since use of a series of mixed solvents corresponds to a gradual change in the relative permittivity of the media and hence in the interactions operative in these solutions. In the present investigation, we have, therefore, utilized conductometry, viscosimetry and volummetry to study the solution behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media.

Sodium carboxymethylcellulose is a chemically modified cellulose derivative (Fig. 4) with large water solubility, broadly used due to its low cost, lack of toxicity, and biodegradability. Food industry, cosmetics, pharmaceuticals, suspension agents, formulation agents in controlled release of drugs and pesticides, papers and paper products, adhesives, and ceramics provide a brief list of the numerous applications where carboxymethylcellulose is used in the acid or in the sodium salt form

As pointed out earlier, the main factors that govern the dissolved state of polyelectrolytes in solutions are firstly, the electro-repulsive forces working between ionic sites in the polymer chain and secondly, the interactions between the polyions and counterions surrounding the polyion chains. The first factor is concerned with expansibility of the polymer chains, whereas the second is not only reflected in counterion binding but also in the amount of solvation and the solvent structure in the vicinity of polyelectrolytes. Both of these factors are related to the relative permittivity of the solvent media. Use of a series of mixed solvents corresponds to the systematic change in the relative permittivity of the media. In this study, the mixed solvent methanol-water has been used. Methanol-water solutions are among the most extensively studied of all solvent mixtures.[100,107,165-175] These mixed solvents are of interest because the two solvents are fully miscible at room temperature and its neighbourhood and the relative permittivities of the mixed solvent media could be varied over a wide range.

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

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Chapter 3

Experimental

Chemicals

Sodium Carboxymethylcellulose

Three sodium carboxymethylcellulose samples with average molecular weights (M_w) of 90,000 [degree of substitution (*DS*) = 0.7], 250,000 [*DS* = 0.9], and 700,000 [*DS* = 0.9] were purchased from Aldrich Chemical Company. The average molecular weights of these

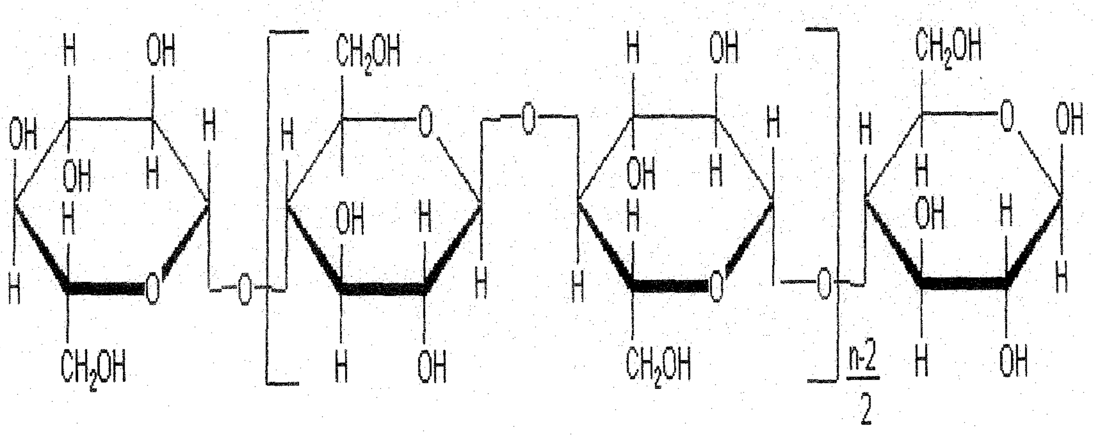

Fig. 1. Diagrammatic representation of a cellulose molecule.

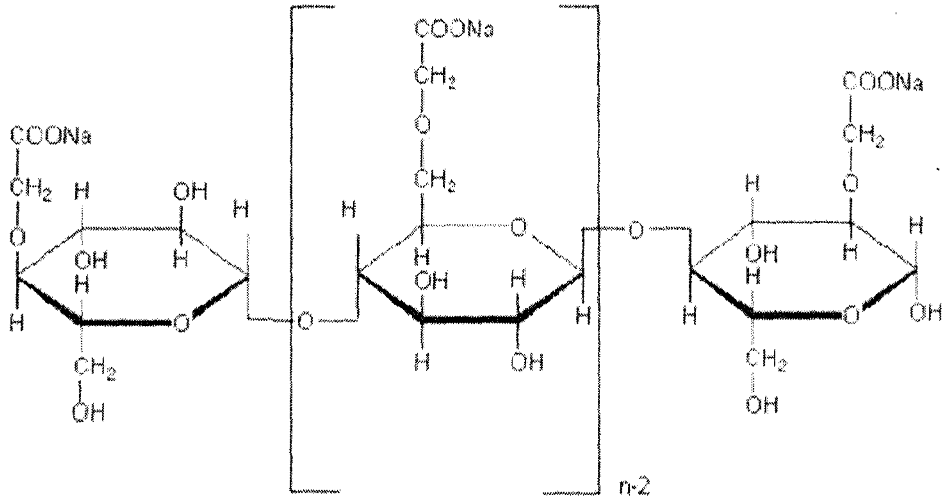

Fig. 2. Sodium carboxymethylcellulose with a degree of substitution of 1.

samples agree well with their viscosity average molecular weights obtained in presence of 0.1 N NaCl using the Mark-Houwink constants from the literature.[1] The degrees of substitution of these samples obtained using a conductometric procedure as described by Eyler *et al.*[2] are also found to be in good agreement with those declared by the manufacturer. The representative Figure 1 displays the Fourier Transform Infrared (FTIR) spectrum of one of the sodium carboxymethylcellulose samples used (M_w = 90,000) in the present study and Table 1 gives the assignments of the important peaks observed.[3]

Salts

Sodium chloride, sodium bromide, potassium chloride, and barium chloride were of Fluka purum or puriss grade; these were dried *in vacuo* for a prolonged period immediately before use and were used without further purification.

Methanol

Methanol (Acros Organics, 99% pure) was distilled twice. The middle fraction was collected and redistilled.The purified solvent had a density of 0.77728 g.cm^{-3} and a coefficient of viscosity of 0.4747 mPa.s at 308.15 K; these values are in good agreement with the literature values.

Water

Triply distilled water was used for the preparation of the experimental solutions. Water was first deionized and then distilled from an all glass distilling set using alkaline $KMnO_4$ solution. The distilled water was then distilled twice. Precautions were taken to prevent contaminations from CO_2 and other impurities. The triply distilled water which had a specific conductance of less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the solutions.

Preparation of the Mixed Solvents

The methanol-water mixed solvents were prepared accurately by mixing requisite amounts of methanol 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 298.15, 308.15, 318.15, and 328.15 K are reported in Table 1. The relative permittivities of methanol-water mixtures at the experimental temperatures were obtained with the equations as described in the literature[4] using the literature density and relative permittivity data of the pure solvents[5, 6] and the densities of the mixed solvents given in Table 1.

Methods

Fourier Transform Infrared (FTIR) Spectral Measurements

The spectrum of sodium carboxymethylcelulose was recorded in the 4000-400 cm^{-1} range at a resolution of 1 cm^{-1} with a Shimadzu 8300 FTIR spectrophotometer using the potassium bromide disk sampling technique.

The characteristic peaks are given in Table 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 1.14 cm^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers[7] using aqueous potassium chloride solution. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

Density Measurements

The densities were measured with an Ostwald-Sprengel type pycknometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycknometer was calibrated at the experimental temperatures with deionized distilled water, methanol and acetonitrile. The precisions of the density measurements were always within 3×10^{-5} $g.cm^{-3}$. 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.

Density measurements were also carried out on an Anton Paar DMA-4500M digital precision densimeter. The precision of the density measurements was $3 \cdot 10^{-5}$ $g \cdot cm^{-3}$. Calibration of the densimeter was done at each temperature using dry air under ambient pressure, and deionized triply distilled water.

Viscosity Measurements

The viscometric measurements were performed at 308.15 K using a Schultz-Immergut-type viscometer[8] 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.[9,10] 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.

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

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Table 1. FTIR Peak Assignments for Sodium Carboxymethylcellulose

Peak position (cm^{-1})	Assignment
3436.50	O-H stretch
2925.93	CH_2 stretch (asymmetric)
1602.08	COO^- (asymmetric)
1420.37	COO^- (symmetric)
1060.70	C-O stretch (RCH_2OH)

Table 2. Densities, ρ (g.cm^{-3}), Coefficients of Viscosities, η_0 (mPa.s) and Relative Permittivities (*D*) of Methanol-Water Mixtures Containing 10, 20 and 30 Volume Percent of Methanol at Different Temperatures

T (K)	ρ (g.cm^{-3})	η_0 (mPa.s)	D
	10 Vol% Methanol		
298.15	0.98297	1.0844	75.09
308.15	0.97973	0.8665	71.57
318.15	0.97604	0.7020	68.18
	20 Vol% Methanol		
298.15	0.96963	1.3106	71.61
308.15	0.96632	1.0217	68.14
318.15	0.96162	0.8075	64.80
328.15	0.95841	0.5306	61.43
	30 Vol% Methanol		
298.15	0.95620	1.4712	67.65
308.15	0.95160	1.1418	64.25
318.15	0.94626	0.8957	60.99
	Methanol		
298.15	0.78659	0.5446	32.66
308.15	0.77728	0.4747	30.74
318.15	0.76774	0.4185	29.92

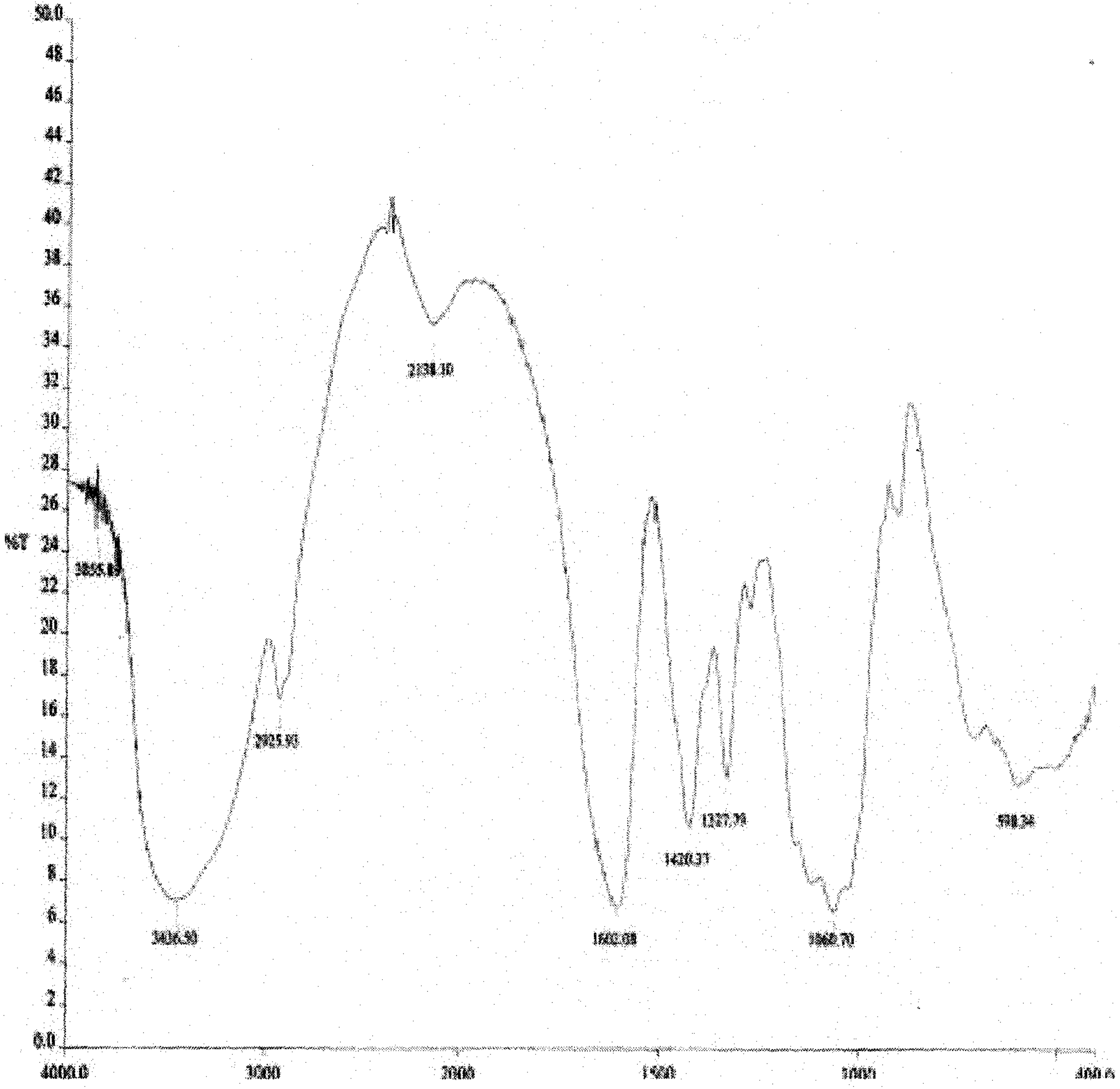

Fig. 1. FTIR spectrum of sodium carboxymethylcellulose.

Chapter 4

Polyion-Counterion Interaction Behaviour for Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media: Effects of Temperature, Medium and Polymer Concentration

Introduction

Polyelectrolytes are macromolecules with many ionizable groups, which in polar solvent media dissociate into a polyion and counterions of opposite charge.[1,2] The thermodynamic and transport properties of polyelectrolytes in solutions are mainly controlled by the interactions between the polyion and counterions. For example, the transport properties, studied by electrical conductivity, are of central importance in accounting for the solution behavior of polyelectrolytes because the electrical conductivity takes into account the movement of any charged entity present in the system under the influence of an externally applied electric field. Current interest in charged polymer solutions is also supported by the needs of biophysics since biopolymers are charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behavior.[3]

Although the electrical conductivity has so far been measured for a great variety of polyelectrolytes,[4-13] only a few studies reported the influence of medium and temperature on the interaction between a polyion and its counterions derived from conductivity measurements.[14-17] We have, therefore, initiated a program to investigate the behavior of different polyelectrolytes in various mixed solvent media as a function of temperature.[18-21] Here we present a study on the electrical conductivity of the semidilute solutions of sodium carboxymethylcellulose in methanol-water mixed solvent media at different temperatures and the data have been analyzed on the basis of the Manning counterion condensation theory as well as the model derived from the scaling concept. The objective of this contribution is to examine the influence of the polymer concentration, the temperature and the medium on (i) the fractions of uncondensed counterions, (ii) the polyion equivalent conductivities, (iii) the standard state free energies of counterion association, and (iv) the solvodynamic friction coefficients of the polyion in the solution to provide a comprehensive understanding of the counterion condensation phenomena in polyelectrolyte solutions. The results are discussed from the viewpoint of the general solution behavior of polyelectrolytes.

Theory

Generally, the equivalent conductivity (Λ) of polyelectrolyte solutions is given by Manning[24]

$$\Lambda = f(\lambda_c^0 + \lambda_p) \tag{1}$$

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 fraction of uncondensed counterions.

The description of different electrical properties of polyelectrolytes in solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory.[22-24] In this model, the polyion is represented by an infinitely long charged line. The small counterions are assumed to form an ionic atmosphere whose density depends on the frame of the polyion and their interactions with the charged polyions are purely Coulombic in nature, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye-Hückel approximation. The solvent is assumed to be a dielectric continuum characterized by a spatially uniform relative permittivity ε. Interactions among the polyions are neglected, the theory being addressed to highly diluted solutions.

According to the Manning counterion condensation theory, polyelectrolytes have been characterized by a linear charge density parameter defined by[23,24]

$$\xi = \frac{e^2}{\varepsilon k_B T b} \tag{2}$$

where e is the protonic charge, ε the relative permitivity of the medium, k_B the Boltzmann constant and T the absolute temperature and b the contour distance per unit charge. This theory states that if $\xi > 1$, enough counterions condense on to the polyion chain to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value.

Considering the electrophoretic and relaxation contributions to the equivalent conductivity, Manning[24] theoretically derived the equivalent conductivity of a polyion, λ_p, with counterions each bearing a charge of z_c

$$\lambda_{\mathrm{p}} = \frac{279A|z_{\mathrm{c}}|^{-1}|\ln \kappa a|}{1 + 43.2A(|z_{\mathrm{c}}|\lambda_{\mathrm{c}}^{0})^{-1}|\ln \kappa a|} \tag{3}$$

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

$$A = \frac{\varepsilon k_B T}{3\pi\eta_0 e} \tag{4}$$

with η_0 being the coefficient of viscosity of the solvent. In Eq. (3), κ is the Debye screening constant, which is defined by

$$\kappa^2 = \frac{4\pi e^2 \xi^{-1} c|z_{\mathrm{c}}|}{\varepsilon k_{\mathrm{B}} T} \tag{5}$$

where c is the stoichiometric equivalent polyion concentration.

In accordance with this model, the equivalent conductivity (Λ) is given by Eq. (2) in conjunction with Eq. (3) with f being defined as

$$f = \frac{0.866}{\xi} \tag{6}$$

Since the Manning theory applies, as stated above, to highly diluted systems where polyion-polyion interactions are assumed to be absent and to polyions modeled as a linear array of point charges, its validity is limited to very low concentration regimes of polyelectrolyte solutions. In most of the earlier studies on the electrical conductivity of polyelectrolyte solutions,[4-19,21,33] the concentrations are far from being very dilute and are primarily the semidilute solutions (c > overlap concentration, c^*) have been studied. The application of the Manning model to these systems is, however, less straightforward because these semidilute polyions do not assume a fully stretched conformation in solution. Careful measurements[4,6-10,14,21] of the electrical conductivity of aqueous salt-free polyelectrolyte solutions, however, demonstrated a major deviation from the Manning theory. In the case of semidilute polyelectrolytes, the polyion concentration modifies the flexibility of the chain, giving rise to different conformational aspects and hence the Manning model is not applicable to these systems.

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been recently proposed by Colby *et al.*[25] using the scaling description put forward by Dobrynin *et al.*[26] for the configuration of a polyelectrolyte chain.

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 $q_\xi = z_c efg$ (z_c 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 $Q_p = N_\xi\ q_\xi = z_c efg\ N_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size 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.

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

$$\lambda_p = \frac{Fz_c efc\xi_0^2}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right) \tag{7}$$

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

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

Within this model, the parameter f - that defines the fraction of uncondensed counterions in the Manning sense - has been treated as an adjustable quantity. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration, the Colby model can be applied to more concentrated systems, up to the concentration c_{D}, where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size. This new model has been applied, so far, to a limited number of aqueous salt-free polyelectrolyte solutions[25,27] and there has, so far, been only one report[33] by our group on the application of this model to a polyelectrolyte dissolved in methanol-water mixed solvent media, and the good agreement with the experiment is very encouraging. Moreover, this model has been successfully employed to identify concentration regimes differing in the fractions of uncondensed counterions.[28]

Experimental

Materials

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance < 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the solvent mixtures. The physical properties of methanol-water mixtures used in this study at 298.15, 308.15, 318.15 and 328.15 K, namely the coefficients of viscosity (η_0), and the relative permittivities (ε), are reported in Table 1. Also included in this table are the limiting equivalent conductivities of the counterion (Na^+), λ_{c}^{0} in methanol-water mixtures containing 10, 20, and 30 volume percent of methanol taken from the literature[34]. Sodium carboxymethylcellulose employed in this investigation was purchased from Aldrich Chemical Company, Inc. The sample had an average molecular weight (M_{w}) of 90,000 and a degree of substitution of 0.70. It was characterized as described earlier by us.[29]

Conductance Measurements

Conductance measurements were carried out on a Pye Unicam PW 9509 conductivity meter at a frequency of 2000 Hz with negligible polarization effects using a dip-type cell with a cell constant of 1.14 cm^{-1} and having an uncertainty of 0.01%. 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.[30] Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium (κ_0) from those of the polyelectrolyte solutions (κ).

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

Viscosity Measurements

The kinematic viscosities (v) were measured by means of a suspended level Ubbelohde viscometer in a water thermostat controlled to 0.01 K. The kinematic viscosities were converted into the absolute viscosities (η) using the density values measured with an Anton Paar DMA 4500 M densitimeter as described earlier by us.[31]

Results and Discussion

Experimental Equivalent Conductivity

Figs. 1a and 1b display the variation of the equivalent conductivity of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol-water mixtures (containing 10, 20, and 30 volume percent of methanol) at 308.15, and 318.15 K respectively over the entire concentration range investigated. The representative figure (Fig. 1c), on the hand, shows the polyelectrolyte concentration dependence of the equivalent conductivity in a given mixed solvent medium (20 volume percent methanol) at 298.15, 308.15, 318.15 and 328.15 K. The equivalent conductivities exhibit a slight increase with decreasing polymer concentration. Figs. 1a and 2b demonstrate a decrease in the Λ values as the medium gets richer in methanol in going from 10 volume percent to 30 volume percent of methanol in methanol-water mixtures over the entire polyelectrolyte concentration range. The effect of temperature on the equivalent conductivity values, on the other hand, is directly evident from Fig. 1c, where in a given medium, the Λ values are found to increase as the temperature is raised from 298.15 to 328.15 K.

Comparison with the Manning Counterion Condensation Theory

Now we will compare the experimental Λ values with those calculated using the Manning theory. In obtaining the theoretical Λ values, the values of the coefficients of viscosity (η_0), and the relative permittivities (ε) of the methanol-water mixtures used in this study alongwith the limiting molar conductivities of the sodium counterion (λ_c^0) are required. The values of η_0, ε, and λ_c^0 for methanol-water mixtures containing 10, 20, and 30 vol% of methanol at 298.15, 308.15, and 318.15 K have been taken from our earlier study.[18] For 20 vol.% methanol-water mixture at 328.15 K, however, ε was obtained from the literature,[32] while η_0 was measured as described in the experimental section, and λ_c^0 was determined in the present work by measuring the electrical conductivities of sodium bromide, sodium tetraphenylborate, and tetrabutylammonium bromide following the procedure described earlier.[20] The values obtained are $\eta_0 = 0.6640$ mPa.s, and $\lambda_c^0 = 86.20$ S.cm^2.mol^{-1}.

The charge density parameters ξ were calculated from Eq. (2) using the literature value for the length of the monomer unit having one charged group[5] and these are listed in Table 1. The theoretical values of λ_p and hence of Λ, are dependent on a, the radius of the polyion cylinder. For the radius of the assumedly rod-like polymer cylinder, we used a value of 8 A^0 for the present analysis.[5]

Theoretical predictions (lines) based on this model along with the experimental Λ values (points) are shown in Fig. 1.

The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. Deviations of the theoretical values from the experimental values were also noticed earlier for other polyelectrolyte solutions.[8-10,14] The discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies Eq. (3).

The reason for the failure of the Manning model can be understood if one estimates the overlap concentration (c*) for the polymer chain investigated using the following equation[13]

$$c^* = \frac{1}{N_A L^2 a} \qquad (8)$$

where L is the countour length and the other symbols have their usual significance. It is observed that the polymer solutions in the present study are essentially in the semidilute regime where the Manning limiting law does not apply ($c^* \approx 0.0001$ eqv.L^{-1}).

Scaling Theory and the Fractions of Uncondensed Counterions

Since the Manning theory fails to describe the conductivity behavior, we have employed the scaling theory approach of the polyelectrolyte conductivity proposed by Colby *et al.*[25] for semidilute polyelectrolyte solutions for the analysis of the present conductivity data.

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) appearing in Eq. (7) depend upon the quality of the solvent and are, for poor solvents, given by[25]

$$\xi_e = b\left(\xi f^2\right)^{-1/3} \tag{9}$$

$$\xi_0 = (cb)^{-1/2}\left(\xi f^2\right)^{-1/3} \tag{10}$$

For good solvent cases, on the other hand, these are given by[25]

$$\xi_e = b\left(\xi f^2\right)^{-3/7} \tag{11}$$

$$\xi_0 = (cb)^{-1/2}\left(\xi f^2\right)^{-1/7} \tag{12}$$

For the present system, good solvent correlations are always found to provide a better description of the experimental results. In Fig. 1, the predictions in accordance with the Colby model (dashed lines) for the semidilute regime have been compared with the experimental equivalent conductivity data treating the mixed solvent media as a good solvent for sodium carboxymethylcellulose.

Fig. 1, however, reveal that although the scaling theory approach, with only one adjustable parameter - the fraction of uncondensed counterions (*f*) - over the entire concentration range provides a significant improvement over the Manning model, a quantitative description of the experimental results is yet to be achieved. It is thus apparent that the assumption of the independence of the effective charge on a polyion chain of the polymer concentration is no longer valid for the system under investigation.

The deviations of the calculated values from the experimental results clearly demonstrate that the fraction of uncondensed counterions varies with the polyelectrolyte concentration for the system under consideration.

We have, therefore, calculated the fractions of uncondensed counterions from our conductivity data using Eq. (1) in conjunction with Eqs. (7), (9) and (10). The concentration dependence of f thus obtained is shown in Fig. 2. The polyion equivalent conductivities have also been computed on the basis of these f values and are depicted in Fig. 3.

Fig. 2 demonstrates that the fractions of the uncondensed counterions do not remain fixed rather they vary over the concentration range investigated in the present study. It is also observed that a preponderant proportion (53 - 62%) of the counterions remain free in solutions.

Effect of Medium on Counterion Condensation

The measured fraction of uncondensed counterions is found to decrease with increasing methanol content (*i.e.*, with decreasing relative permittivity) of the mixed solvent media at any given temperature over the entire concentration range investigated (Figs. 2a and 2b). Since decreasing relative permittivity should result in a greater interaction between the polyion and counterions, the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower - as has been observed in the present study.

Effect of Temperature on Counterion Condensation

The fraction of uncondensed counterions is found to decrease with increasing temperature over the entire polyelectrolyte concentration range in a given mixed solvent medium (*cf.* Fig. 2c). A plausible explanation for this observation might be sought in a change in solvation and condensation behavior of counterions upon changing the temperature. Raising the temperature has the effect of gradual desolvation for the counterions and the polyions which results in an increase of counterion condensation on the polyion chain. This is reflected in the decreasing fraction of uncondensed counterions at higher temperatures. Desolvation of the sodium counterions with increasing temperature is directly evident from our earlier investigation where we noted a significant increase in their mobility with temperature.[34] This has been ascribed to the decreasing size of their solvodynamic entity and hence to an increasing surface charge density resulting in a greater mobility under the action of the applied electric field. A similar behavior was also observed for aqueous solutions of sodium and potassium dextran sulfates[35] where an increase in the charge density parameter (and hence, according to Eq. (6), a decrease in the fraction of uncondensed counterions) was reported with the rise of temperature. Similar results were observed with sodium carboxymethylcellulose[21] and sodium polystyrenesulfonate[33] in mixed-solvent media earlier.

Effect of Medium on Polyion Equivalent Conductivity

Figs. 3a and 3b show that the polyion equivalent conductivity decreases with increasing methanol content of the mixed solvent media at any given temperature. More counterion condensation onto the polyion chain with decreasing relative permittivity of the medium causes a reduction in the effective charge (effect 1) and hence a contraction of the polyion coil (effect 2). Decreasing relative permittivity, on the other hand, is expected to increase the intrapolyionic repulsion leading to a stretching of the coil (effect 3). The first and the third effects should result in a lower polyion mobility, while the second in a higher mobility as the medium becomes richer in methanol. The present results demonstrate the predominance of the combined influence of the first and the third effects over the second.

Effect of Temperature on Polyion Equivalent Conductivity

The polyion equivalent conductivity is found to increase with increasing temperature in a given medium (Fig. 3c). More counterion condensation onto the polyion chain with increasing temperature (*cf. 4.6*) causes a reduction in the effective charge (effect 1) and hence gives rise to a contraction of the polyion coil (effect 2). Again an increase in the temperature lowers the relative permittivity of the medium, which is expected to increase the intrapolyionic repulsion leading to a stretching of the coil (effect 3). A fourth effect is a temperature-induced increase in the polyion equivalent conductivity. The first and the third effects should result in a lower polyion mobility, while the second and the fourth in a higher mobility as the medium becomes richer in methanol. The present results demonstrate the predominance of the combined influence of the first and the third effects over that of the second and the fourth.

The Association Constant (K_A) and the Standard State Free Energies of Counterion Condensation (ΔG_A^0) and their Variation with Polyelectrolyte Concentration, Solvent Medium, and Temperature

In order to obtain an insight into the spontaneity of the counterion condensation process, an information on the standard state free energies of counterion association (ΔG_A^0) is essential. For this purpose, the values of the association constants (K_A) for the binding of the counterions onto to polyionic sites defined as the equilibrium constant for the reaction

$$\text{Free site} + \text{Na}^+ \Leftrightarrow \text{Combined site} \qquad (13)$$

have been calculated as a function of concentration from the fractions of uncondensed counterions using the following equation:

$$\ln K_A = \ln\left(\frac{1-f}{f}\right) - \ln(fc) \qquad (14)$$

The standard state free energies of counterion association (ΔG_A^0) can then be easily obtained from:

$$\Delta G_A^0 = -RT \ln K_A \qquad (15)$$

where R is the universal gas constant.

Figs. 4a and 4b display the variation of ΔG_A^0 values of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol-water mixtures containing respectively 10, 20, and 30 volume percent of methanol at 298.15 and 308.15 K over the entire concentration range investigated. Fig. 4c, on the other hand, shows the polyelectrolyte concentration dependence of the ΔG_A^0 values in a given mixed solvent medium at different temperatures. The negative

$\Delta G_{\mathrm{A}}^{0}$ values indicate that the counterion condensation process is spontaneous for the present polyelectrolyte system over the entire concentration range although the process becomes less spontaneous as the concentration increases. Addition of increasing amount of methanol to the medium makes the counterion condensation process more favorable. The spontaneity of the counterion condensation process is, also, found to increase as the temperature increases in a given mixed solvent medium (Fig. 4c).

The Coefficient of Friction between the Polyion and the Solvent (f_{ps}) and its Variation with Polyelectrolyte Concentration, Solvent Medium and Temperature

The friction coefficient provides a measure of the friction between a monomer unit of the polyion and the solvent and can be estimated from the expression[36]

$$f_{\mathrm{ps}} = \frac{|z_{\mathrm{p}}| fF^{2}}{\lambda_{\mathrm{p}}} \tag{17}$$

where z_{p} is the number of elementary charges on the monomer unit of the completely dissociated polyion, and the other symbols have their usual significance. The results are summarized in Figs. 5a-c. Figs. 5a and 5b show the dependence of f_{ps} on $\sqrt{c}$ in 10, 20, and 30 volume percent methanol-water mixtures each at 298.15 and 308.15 K. Influence of temperature on the concentration dependence of the f_{ps} values in a given mixed solvent medium (20 volume per cent) is depicted in Fig. 5c. We can see from the coefficients of friction of the carboxymethylcellulose ion (Fig. 5a-c) that the possible conformational changes of the molecules caused by dilution lead to changes in solvodynamic resistance. The effects become more prominent as the temperature is lowered in a given medium, or as the medium becomes richer in the organic solvent at a given temperature. The friction coefficients of the monomer units decrease with increasing temperature over the entire polyelectrolyte concentration range in a given mixed solvent medium thus indicating smaller sizes of the monomer units at higher temperatures. This supports the phenomenon of gradual desolvation of the monomer units inferred earlier. An increase in the friction coefficients with increasing methanol content of the mixture over the entire polyelectrolyte concentration range at a given temperature, on the other hand, reflects bigger sizes of the monomer units as the medium becomes richer in the organic cosolvent.

Conclusions

An investigation on the electrical conductivity of salt-free solution of an anionic polyelectrolyte - sodium carboxymethylcellulose - in methanol-water mixed solvent media has been performed as a function of polymer concentration. The effect of temperature on the electrical conductivity was also investigated. The equivalent conductivities are found to increase with increasing temperature over the entire concentration range in a given mixed solvent medium whereas these are found to decrease as the relative permittivity of the medium decreases. The conductivity theory, proposed by Manning, for salt-free polyelectrolyte solutions, was applied to analyze the experimental data. The measured values of equivalent conductivity could not be quantitatively described by the Manning counterion condensation theory. This discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model valid only at infinite dilution that underlies this theory. A recent model based on the scaling approach for the configuration of a polyelectrolyte chain in semidilute solution has, therefore, been employed to determine the fractions of uncondensed counterions. The influences of the temperature, the medium, and the polymer concentration on (i) the fractions of uncondensed counterions, (ii) the polyion equivalent conductivities, (iii) the standard state free energies of counterion condensation, and (iv) the coefficients of friction between the polyion and the solvent have been interpreted from the viewpoints of polyion-countreion interactions, solvation of counterions and the polyionic sites, and counterion dissociation.

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Table 1. The Charge Density Parameters (ξ) and the Fractions of Uncondensed Counterions (f) for the best-fit of the Experimental Equivalent Conductance for Sodium Carboxymethylcellulose in Methanol–Water Mixed Solvent Media following the Scaling Theory Approach using Good Solvent Correlation along-with the respective Standard Deviations (σ) including the Standard Deviations for the Poor Solvent Correlation

Vol.% of methanol	T(K)	ξ	f	σ (poor solvent)	σ (good solvent)
10	308.15	1.0321	0.61	1.49	0.93
10	318.15	1.0494	0.60	2.29	1.46
20	298.15	1.0661	0.60	0.84	0.56
20	308.15	1.0841	0.59	1.34	0.86
20	318.15	1.1041	0.57	2.51	1.55
20	328.15	1.1276	0.55	2.53	1.56
30	308.15	1.1497	0.55	0.88	0.70
30	318.15	1.1731	0.53	1.14	0.76

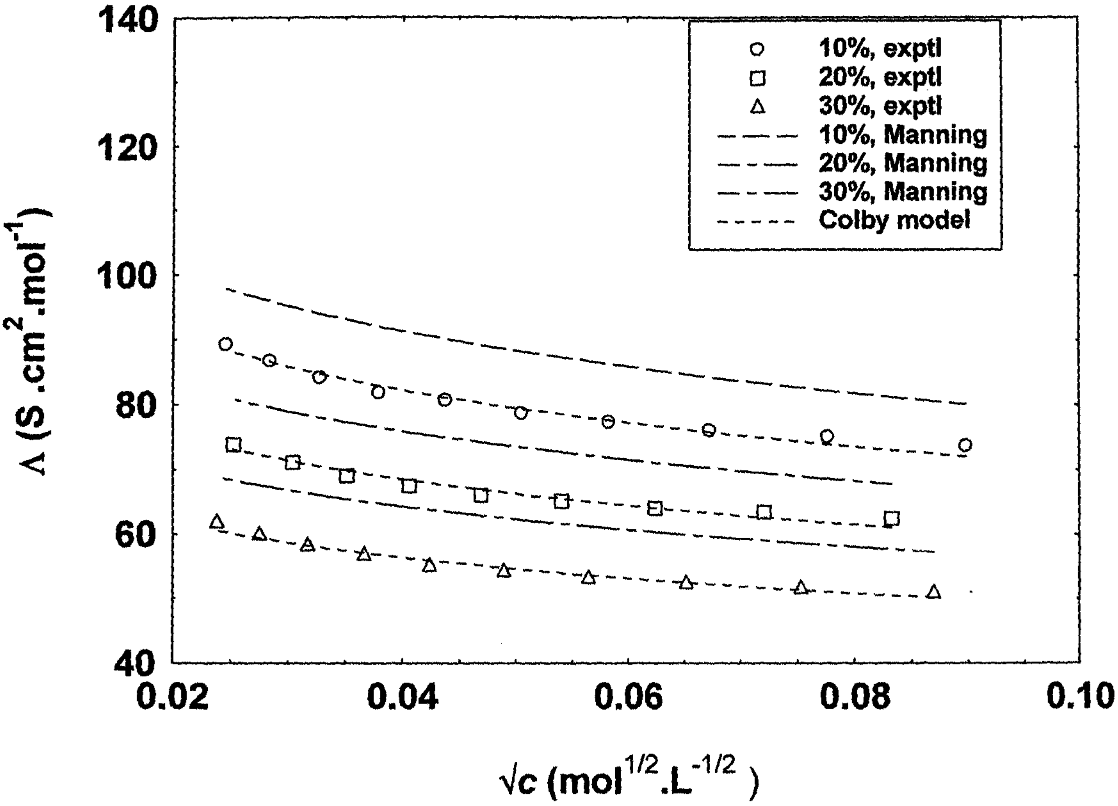

Fig. 1a. Equivalent conductivities (Λ) of sodium carboxymethylellulose as a function of square root of the polymer concentration (√c) at the temperature of 308.15 K, in different methanol-water mixtures.

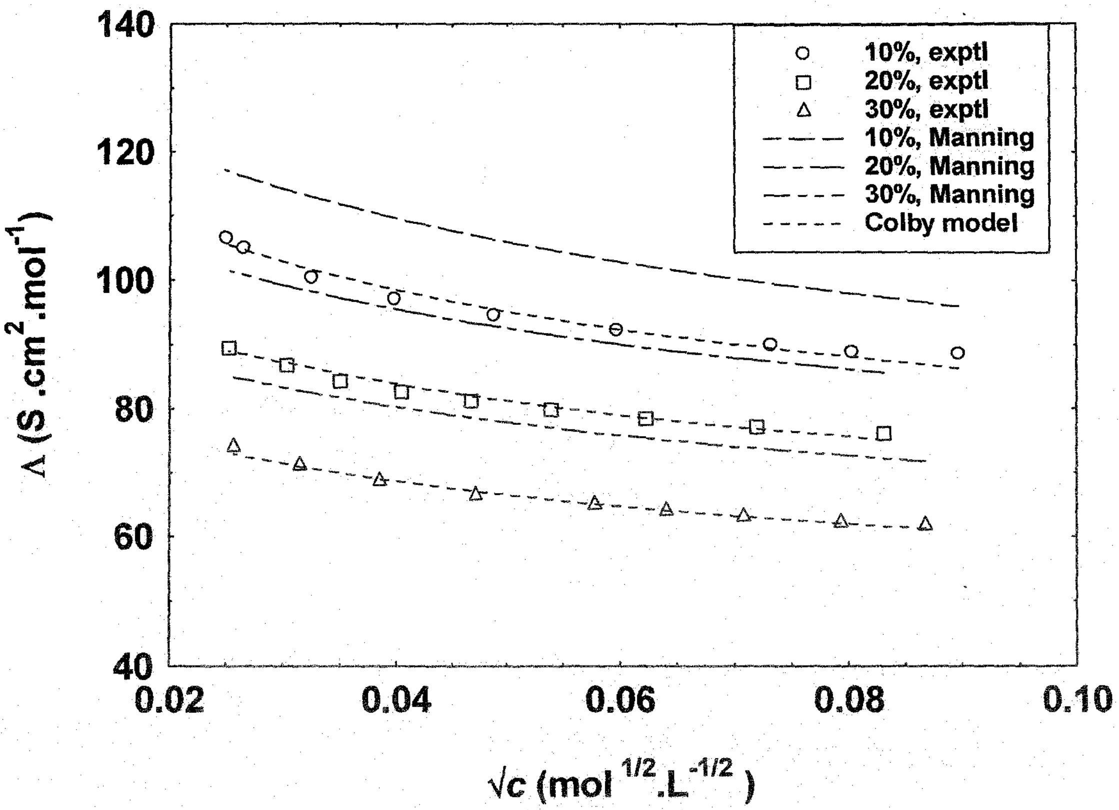

Fig. 1b. Equivalent conductivities (Λ) of sodium carboxymethylellulose as a function of square root of the polymer concentration (√c) at the temperature of 318.15 K, in different methanol-water mixtures.

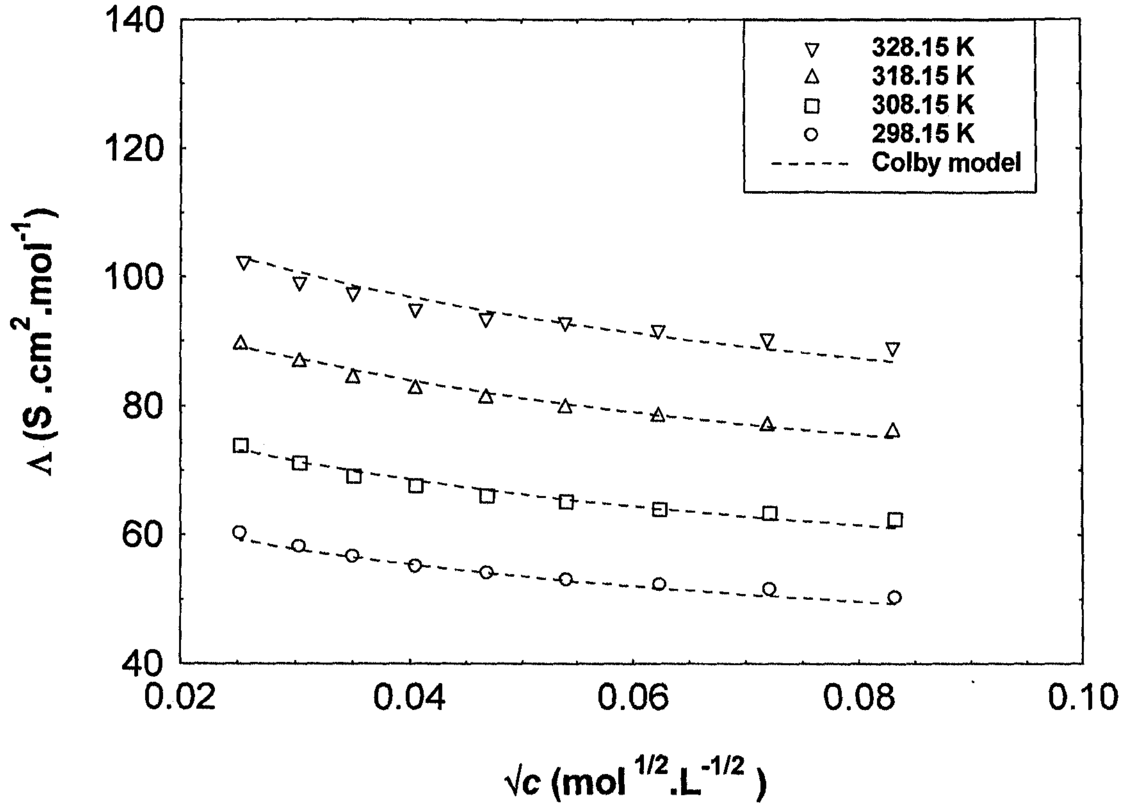

Fig. 1c. Equivalent conductivities (Λ) of sodium carboxymethylellulose as a function of square root of the polymer concentration (√c) at the temperature of 298.15 K, 308.15 K, 318.15 K, and 328.15 K in 20 vol% methanol-water mixtures.

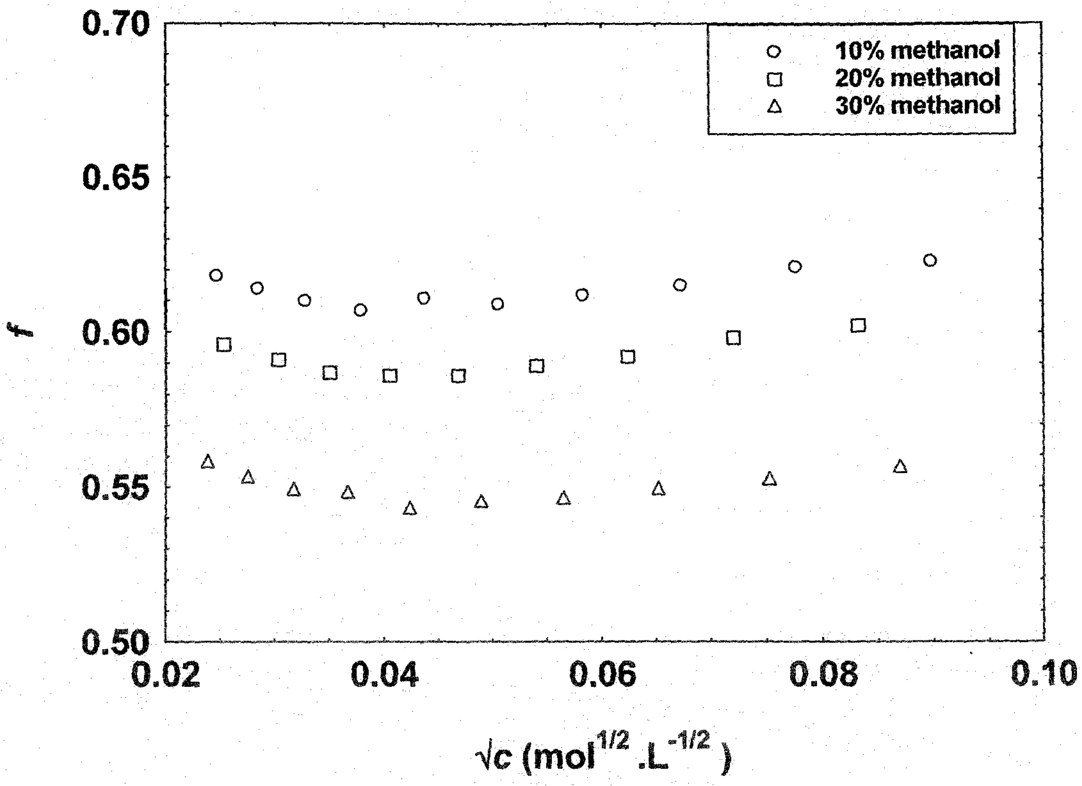

Fig. 2a. Variation of fraction of uncondensed counterions (*f*) of sodium carboxymetylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in three different methanol-water mixtures at 308.15 K.

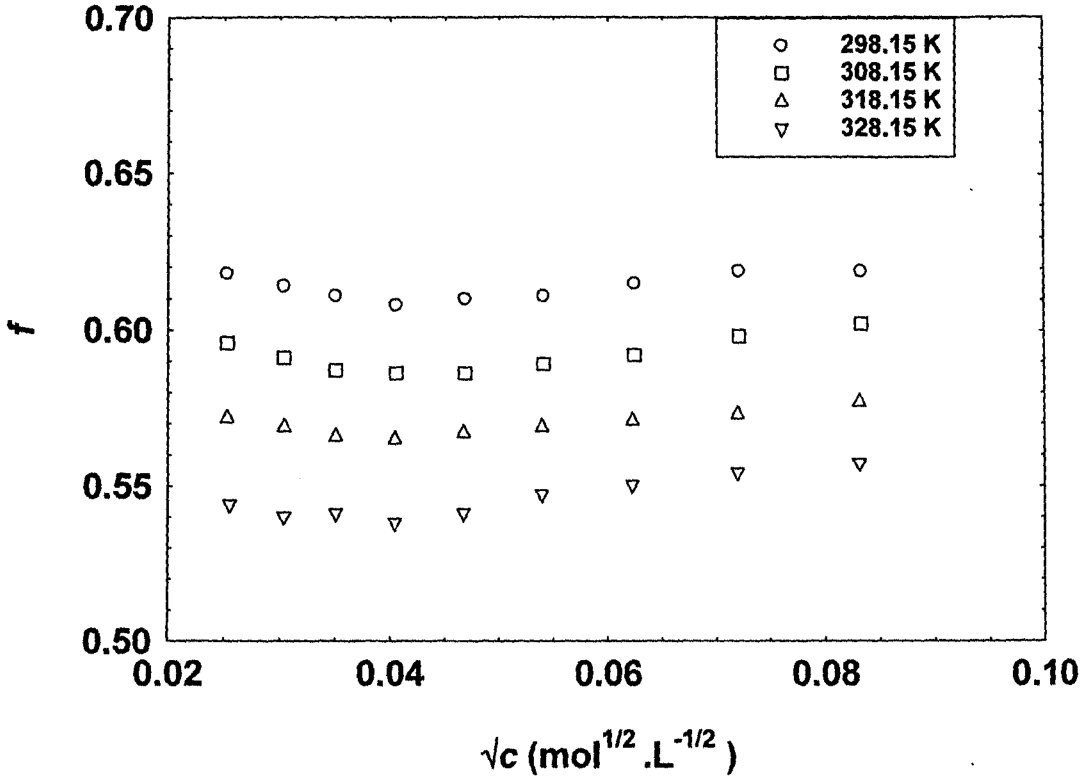

Fig. 2b. Variation of fraction of uncondensed counterions (*f*) of sodium carboxymetylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in three different methanol-water mixtures at 318.15 K.

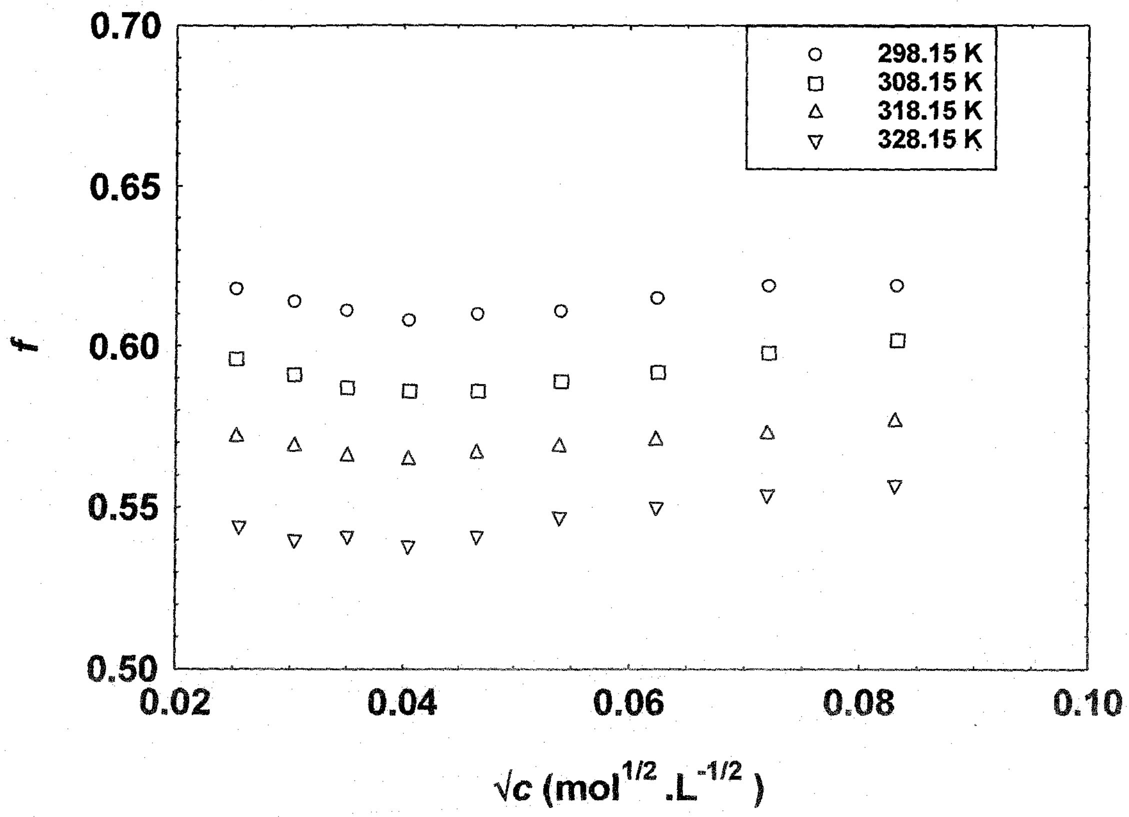

Fig. 2c. Variation of fraction of uncondensed counterions (*f*) of sodium carboxymetylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in 20 vol% methanol -water mixtures at four different temperature.

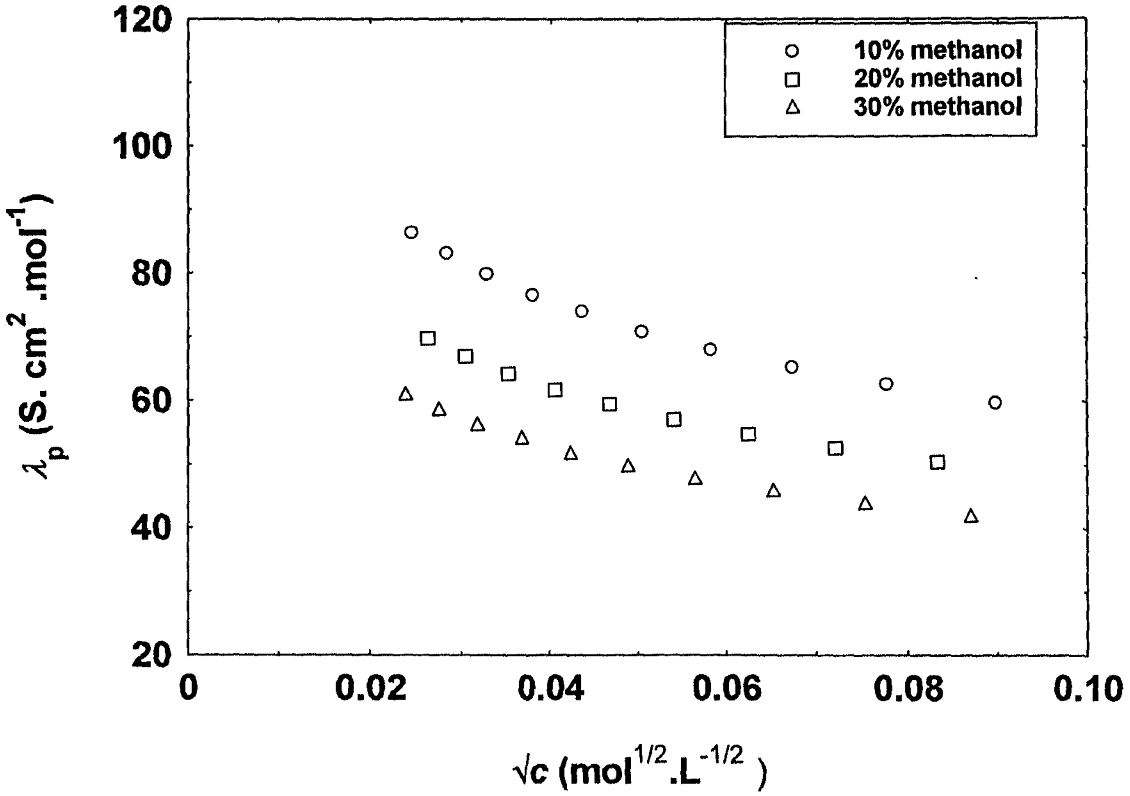

Fig. 3a. Variation of the polyion molar conductivity (λ_p) of sodium carboxymethylcellulose solution as a function of square root of polyion concentration (√c) in three different methanol-water mixture at 308.15 K.

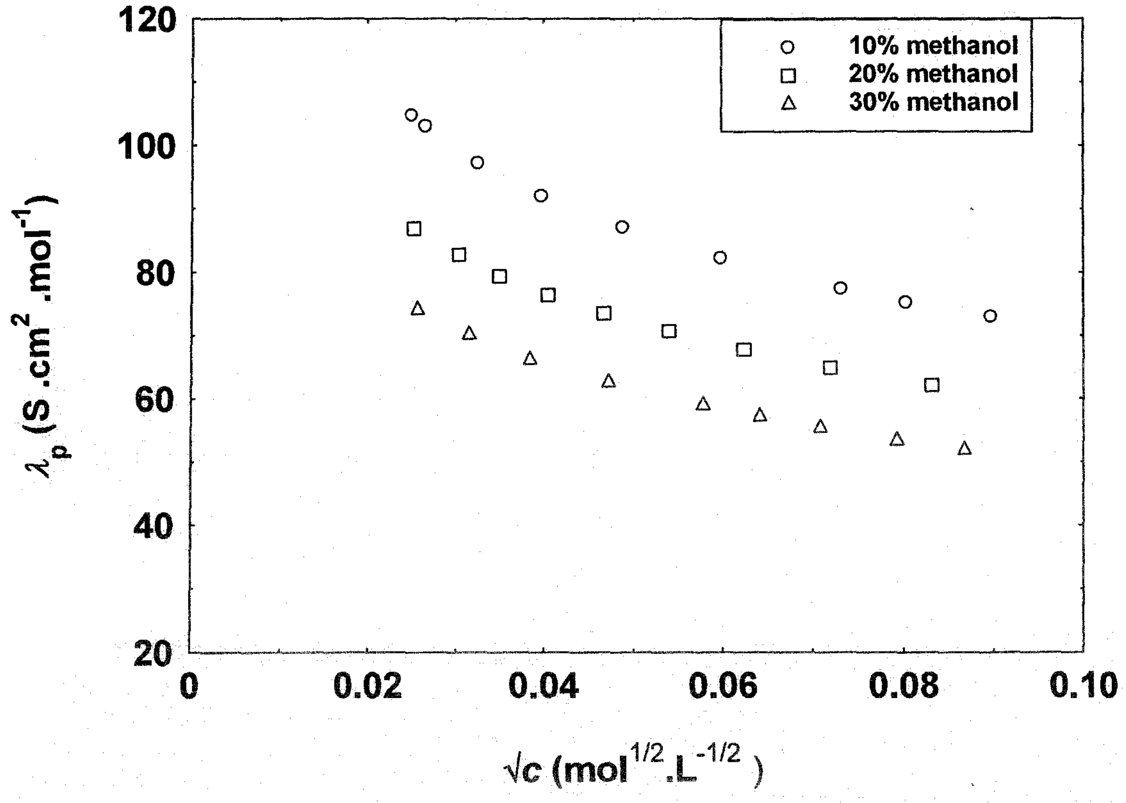

Fig. 3b. Variation of the polyion molar conductivity (λ_p) of sodium carboxymethylcellulose solution as a function of square root of polyion concentration ($\sqrt{c}$) in three different methanol-water mixture at 318.15 K.

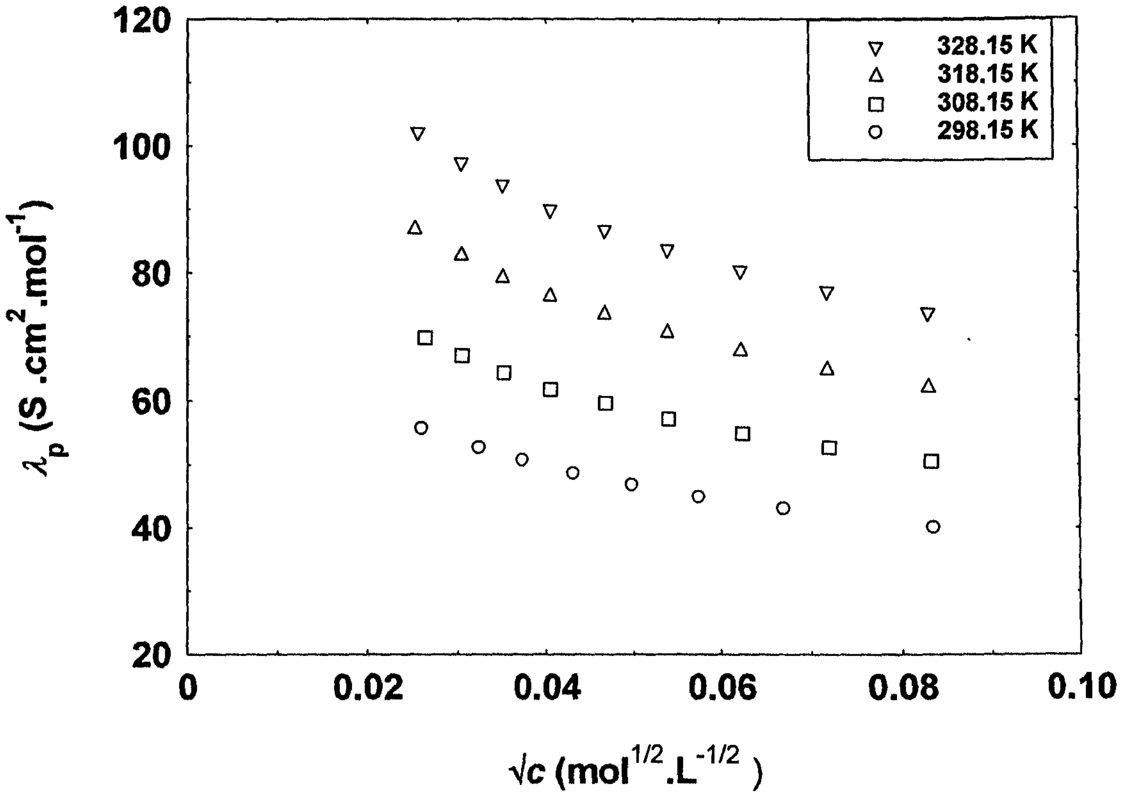

Fig. 3c. Variation of the polyion molar conductivity (λ_p) of sodium carboxymethylcellulose solution as a function of square root of polyion concentration ($\sqrt{c}$) in 20 vol% methanol-water mixture at four different temperature.

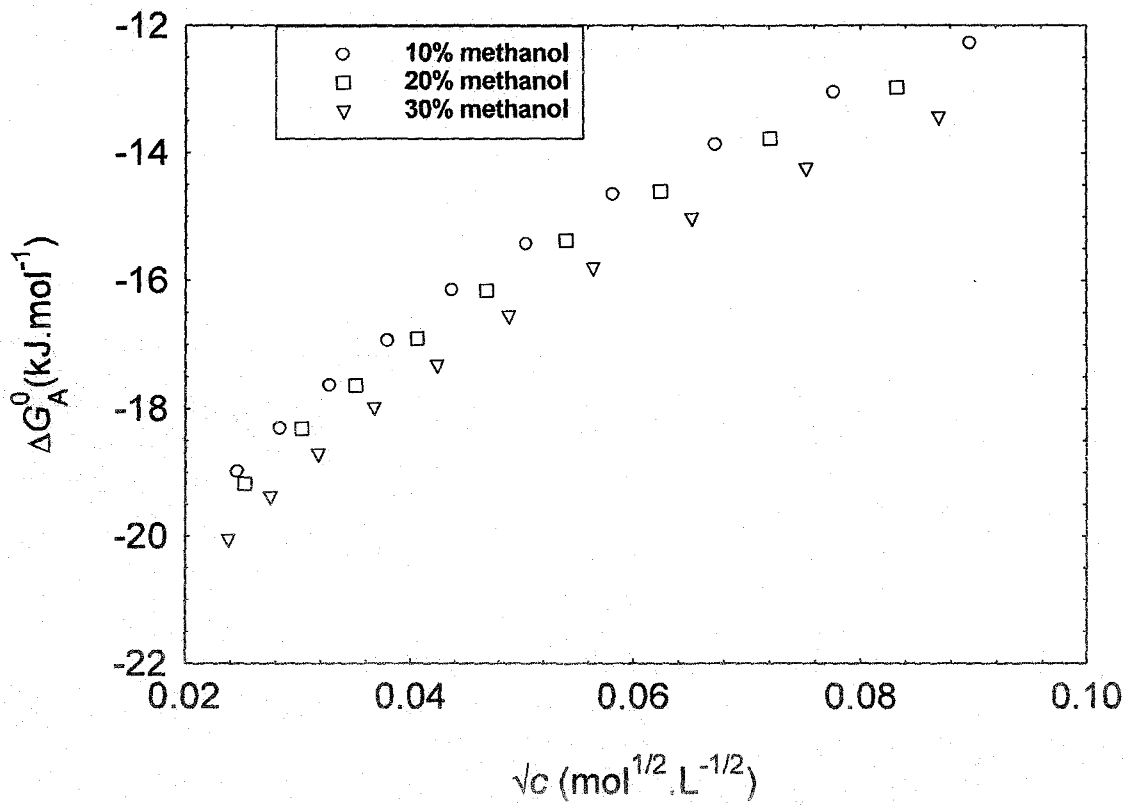

Fig. 4a. Variation of standard state free energies of counterion association (ΔG_A^0) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in three different methanol-water mixtures at 308.15 K.

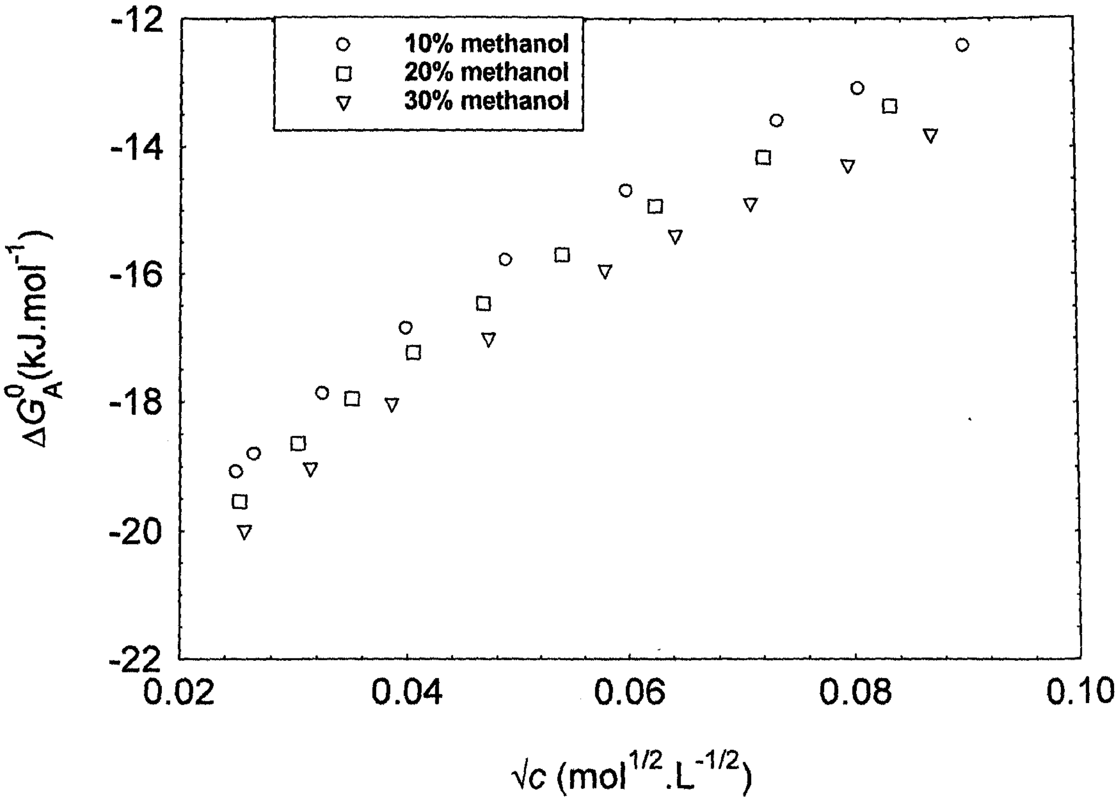

Fig. 4b. Variation of standard state free energies of counterion association (ΔG_A^0) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration ($\sqrt{c}$) in three different methanol-water mixtures at 318.15 K.

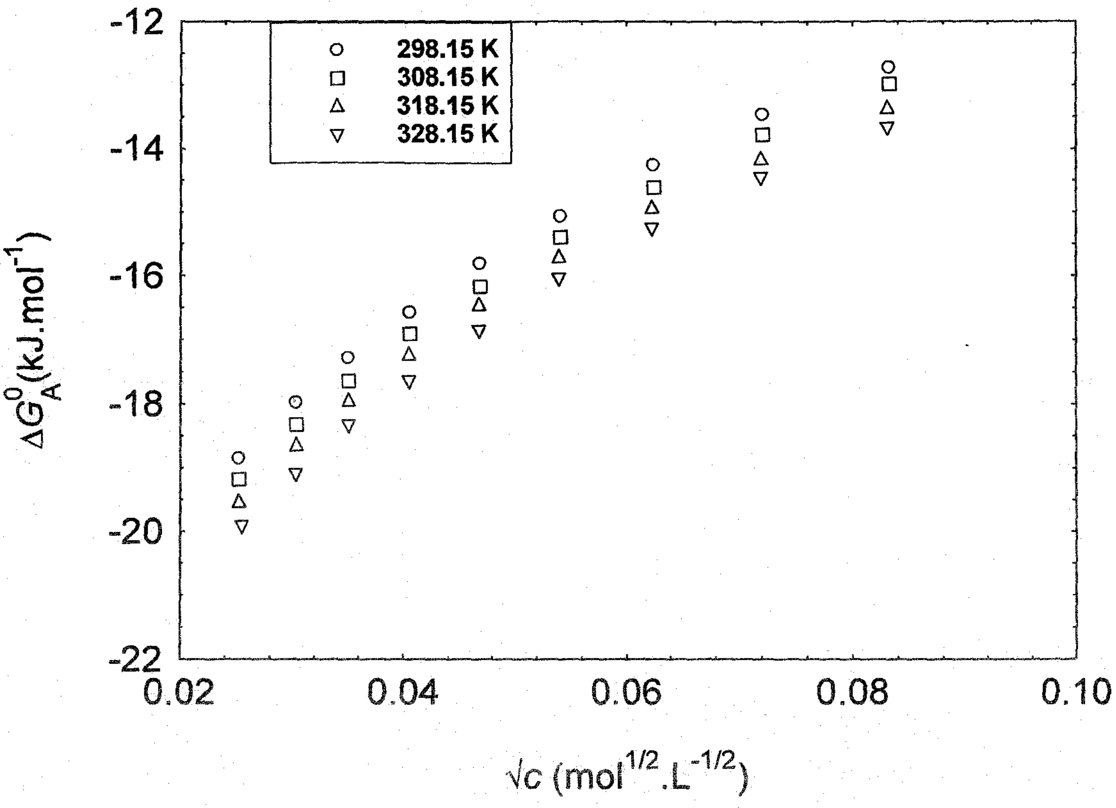

Fig. 4c. Variation of standard state free energies of counterion association (ΔG_A^0) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) for 20 vol% methanol-water mixtures at four different temperature.

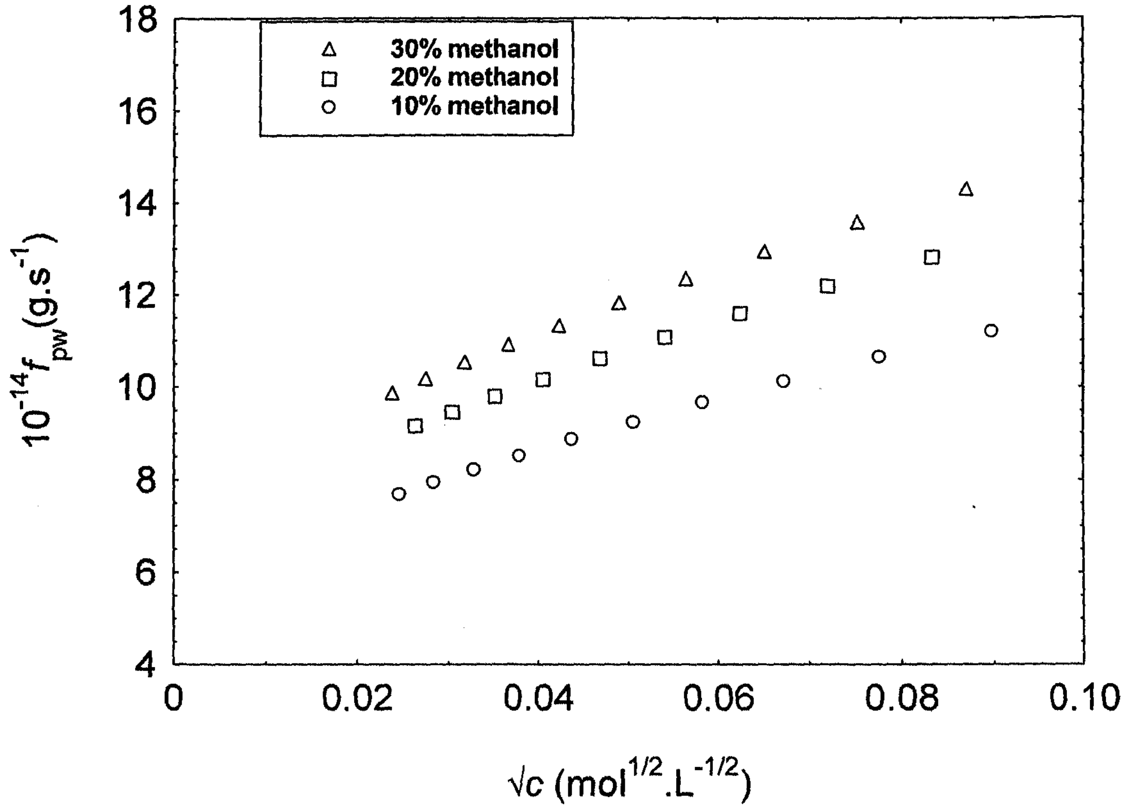

Fig. 5a. Variation of the coefficient of friction between the polyion and solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in three different methanol-water mixtures at 308.15 K.

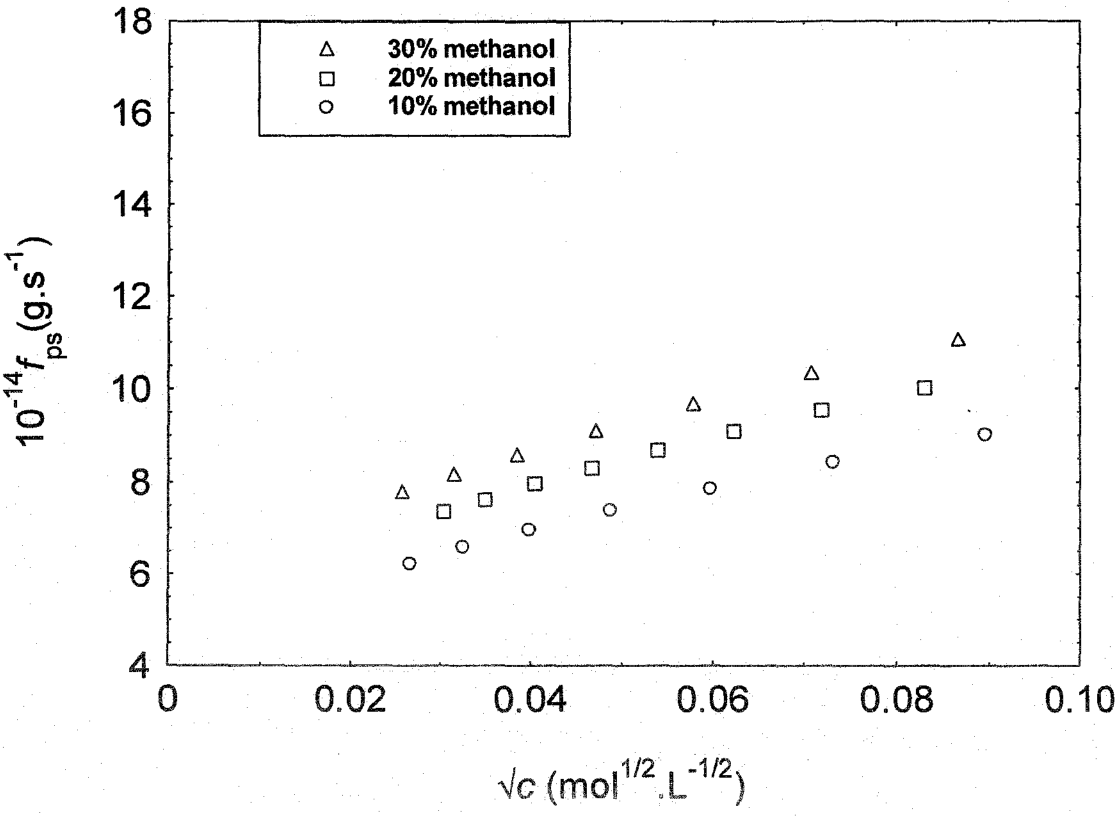

Fig. 5b. Variation of the coefficient of friction between the polyion and solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in three different methanol-water mixtures at 318.15 K.

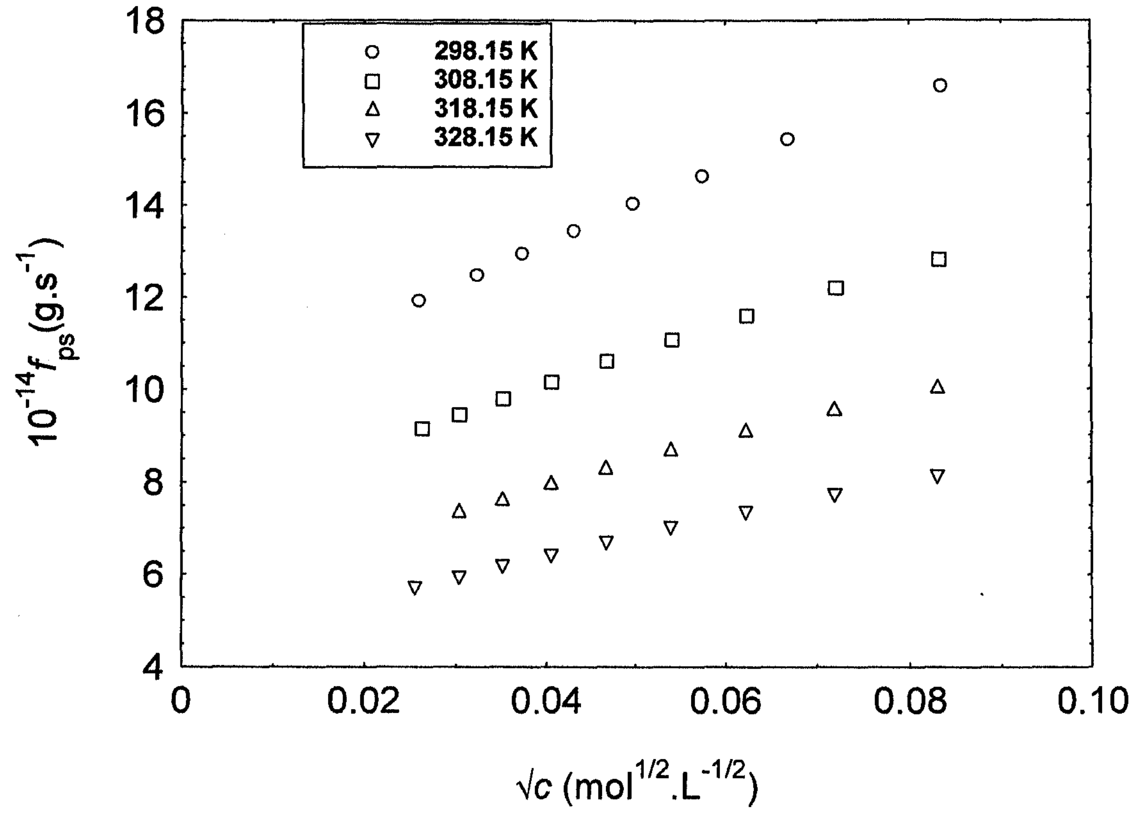

Fig. 5c. Variation of the coefficient of friction between the polyion and solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of square root of polyelectrolyte concentration (√c) in 20 vol% methanol-water mixtures at four different temperatures.

Chapter 5

Effect of Salts on the Conductivity of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media

Introduction

The conductance behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media in absence of an added salt has been reported in Chapter 4. In this chapter, we report the results of conductivity measurements on the solutions of sodium carboxymethylcellulose in methanol-water solvent mixtures in presence of two 1:1 electrolytes *i.e.*, sodium chloride and sodium bromide. The addition of salts to a polyelectrolyte solution can change the behaviour of polyelectrolytes in solution appreciably essentially because of the changed level of counterion condensation and changed conformation of the polyion chains in salt solution, and hence such study can help obtain deeper insight into the polyion-counterion interactions.

Devore and Manning[1] first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory[2] without much success.

In view of the inadequacy of the Manning theory of the electrical transport of salt containing polyelectrolytes 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.[3-7]. Traditionally, this approach takes the form of an assumed additivity of the specific conductances of the polyelectrolyte and the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_{\mathrm{P}} + \kappa_{\mathrm{S}} \qquad (1)$$

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 a polyelectrolyte.

However, these investigations[3-7] 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.*[3,4] 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

$$\kappa = \kappa_p + \kappa_S \left(\frac{D_2}{D_2^0} \right) \tag{2}$$

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 measure[2] of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s \left(D_2 / D_2^0 \right)$.

Although the "modified" additivity has been shown to be somewhat better than the "primitive" one, departures from the experimental results are still prominent.[3-7] Later Bordi *et al.*[8] evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach[9] 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 one of us[10] 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.*[9] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[10] This approach has been extensively tested with data on sodium polystyrenesulfonate in the presence of sodium chloride in 2-ethoxyethanol-water mixed solvent media at different temperatures.[11] It has also been tested on sodium carboxymethylcellulose in presence of sodium chloride in acetonitrile-water mixed solvent media.[12] The data set used considered 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.

In this chapter, we report the results of conductivity measurements on the solutions of an anionic polyelectrolyte sodium carboxymethylcellulose in the presence of sodium chloride and sodium bromide in methanol-water mixtures. The purpose of this study is to apply this new approach to a different polyelectrolyte-solvent system in order to test its general validity and to examine the influences of the medium and the concentration of the added salt on the counterion-condensation behaviour of the polyelectrolyte in the presence of a salt.

Theory

Here we will briefly describe the model which has recently been introduced by one of us to interpret the conductance behavior of polyelectrolyte in presence of salt.[11,12]

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 (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.*,[9] the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

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

where c 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

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

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

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

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.

Experimental

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. The physical properties of the purified solvent was found to be in good agreement with the literature values.[13] Triply distilled water with a specific conductance less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of solvent mixtures. Sodium carboxymethylcellulose employed in this investigation was purchased from Aldrich Chemical Company, Inc. The sample had an average molecular weight (*M*) of 90,000 and a degree of substitution of 0.7. It was characterized in a similar fashion as described earlier by us.[15] The average molecular weight of the sample was estimated from the intrinsic viscosity value determined in 0.2 M NaCl aqueous solution at 298.15 K using the Mark-Houwink equation with the constants obtained from the literature.[15] *DS* was determined by a conductometric procedure as described by Eyler *et al.*[16] These values agree well with those declared by the procedure. Sodium chloride (Fluka) and sodium bromide (Fluka) were of puriss grade. These were dried *in vacuo* for prolonged period immediately before use.

Conductance measurements were carried out on a Pye Unicam PW 9509 conductivity meter at a frequency of 2000 Hz with negligible polarization effects using a dip-type cell with a cell constant of 1.14 cm^{-1} and having an uncertainty of 0.01%. 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.[17,18] Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium (κ_0) from those of the polyelectrolyte solution (κ).

In order to avoid any moisture pick up the solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed in three replicates and the results were averaged.

Results and Discussion

Experimental Specific Conductivity

The specific conductivities of sodium carboxymethylcellulose as a function of the polymer concentration in a given methanol-water mixture with varying amounts of added sodium chloride and sodium bromide are shown in the representative figures (Figs. 1-4). From these figures, it is apparent that for all the solutions studied the specific conductivities increase with polyelectrolyte concentration. The addition of salt increases the specific conductances of the polyelectrolyte-salt system as it should be. The specific conductances of sodium carboxymthylcellulose solutions in any given methanol-water medium are always found to greater in presence of sodium bromide than those measured in presence of sodium chloride. The specific conductances of the polyelectrolyte-salt solution in methanol-water media have been found to decrease with increasing methanol content in the media at constant added salt concentration.

Scaling Theory and the Fraction of Uncondensed Counterions

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) appearing in Eq. (5) depend upon the quality of the solvent and are for poor solvents, given by[12]

$$\xi_e = bf'^{-2}\xi^{-1/3} \tag{6}$$

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

with the charge density parameter ξ defined as

$$\xi = \frac{e^2}{\varepsilon kTb} \tag{8}$$

where b is the spacing between the charged groups taken along the axis of polyion chain, k the Boltzman constant, and T the temperature in the absolute scale. The charge density parameters were calculated using a segment length of 5.15×10^{-8} cm, considering a degree of substitution of 0.7.

For good solvent cases, on the other hand, these are given by

$$\xi_e = b\left(\xi f'^{2}\right)^{-3/7} \tag{9}$$

$$\xi_0 = (cb)^{-1/2}\left(\xi f'^{2}\right)^{-1/7} \tag{10}$$

For the present system, good solvent correlations are always found to provide a better description of the experimental results. In Figs. 1 and 2, the predictions in accordance with the Eq. (5) (dashed lines) have been compared with the experimental specific conductivity data treating the mixed solvent media as a good solvent for sodium carboxymethylcellulose.

The specific conductivity values of the polyelectrolyte-salt system as a function of the polyelectrolyte concentration in a given solvent medium 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 1. In the representative Figs. 1 and 2 we compare the calculated specific conductivities using the f' values reported in Table 1 with those obtained experimentally. From the standard deviations recorded in Table 1, as well as from an inspection of these figures, it is directly evident that the present method of analysis reproduced the experimental results quite satisfactorily. The present experimental results, thus, provide further support in favor of the validity of the model for the conductivity of polyelectrolyte-salt solutions proposed recently by one of us.[11,12]

The results reported in Table 1 demonstrate that a certain proportion of the counterions remain condensed onto the polyion chains in the present system, the fraction of the uncondensed counterions being approximately 43 to 59%. A survey of the literature indicated that, although studies on the electrical conductances for different aqueous polyelectrolyte-salt solutions are available,[3-7,19] in most of the cases the quantification of the countertion condensation was either not attemped[4-7] or was based on Manning counterion condensation model[3,19] which has subsequently been shown to be inappropriate to describe the polyelectrolyte conductivity.[1,21]

Effect of Added Salt Concentration on Counterion Condensation

The fraction of uncondensed counterions has been found to decrease with increasing concentration of the added salts. This indicates that addition of salt to the present polyelectrolyte solutions promotes counterion binding onto the polyion chains. This is clear from the data sets which are given in Table 1.

Effect of Medium on the Counterion Condensation

Measured fraction of uncondensed counterions is found to decrease with increasing methanol content (*i.e.*, with decreasing relative permittivity) of the mixed solvent media over the entire concentration range investigated. Since decreasing relative permittivity should result in a greater interaction between polyion and counterions, the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower as has been observed in the present study.

Effect of Added Salt Concentration on Polyion Conductivity

Polyion conductivities have been found to decrease with the increase in the added salt concentration for both the salt solutions. As pointed out above, addition of a salt to the present polyelectrolyte system causes more counterion condensation. This obviously reduces the overall charge on the polyion chains and thus a contraction of the polyion coils is expected upon addition of an external salt. Reduced charge on the polyion chains reduces the polyion conductivity, whereas the reduced size of the polyion coils enhances it, and the balance between these two opposing effects controls the polyion conductivity. The present experimental results demonstrate that the charge effect predominates over the size effect for the system under investigation. This phenomena has been represented in Figs. 3 and 4.

Effect of Medium on the Polyion Conductivity

Fig. 5 show that the polyion conductivity decreases with increasing methanol content of the mixed solvent media. More counterion condensation onto the polyion chain with decreasing relative permittivity of the medium causes a reduction in the effective charge (effect 1) and hence a contraction of the polyion coil (effect 2). Decreasing relative permittivity, on the other hand, is expected to increase the intra-polyionic repulsion leading to a stretching of the coil (effect 3). The first and the third effects should result in lower polyion mobility, while the second in a higher mobility as the medium becomes richer in methanol. The present results demonstrate the predominance of the combined influence of the first and the third effects over the second. These results are in accordance with the previous results obtained by study in absence and presence of added salt.[11,12,20,22-24]

The nature of variations is seen to be similar in absence of any added salt which has been discussed earlier.

The Association Constant (K_A) and the Standard State Free Energies of Counterion Condensation (ΔG_A^0) and their Variation with Polyelectrolyte Concentration, Solvent Medium, and Added Salt Concentration

In order to obtain an insight into the spontaneity of the counterion condensation process, an information on the standard state free energies of counterion association (ΔG_A^0) is essential. For this purpose, the values of the association constants (K_A) for the binding of the counterions onto to polyionic sites defined as the equilibrium constant for the reaction

$$\text{Free site} + \text{Na}^+ \Leftrightarrow \text{Combined site} \tag{11}$$

have been calculated as a function of concentration from the fractions of uncondensed counterions using the following equation[20]

$$\ln K_A = \ln\left(\frac{1-f}{f}\right) - \ln(fc) \tag{12}$$

The values of the association constants (K_A) thus calculated have been found to increase with decreasing concentration of the polyelectrolyte. The influences of different variables on K_A have been shown in Figs. 6-8.

The association constant values are found to increase as the methanol-water mixed solvent medium becomes richer in methanol at a constant level of the added salt concentration. These are also found to increase as the concentration of the added salt is gradually increased in a given mixed solvent medium.

The standard state free energies of counterion association (ΔG_A^0) can then be easily obtained from:

$$\Delta G_A^0 = -RT \ln K_A \tag{15}$$

where R is the universal gas constant.

Figs. 9 -11 display the variation of ΔG_A^0 values of sodium carboxymethylcellulose solutions as a function of the polyelectrolyte concentration in three different methanol-water mixtures containing respectively 10, 20, and 30 vol.% of methanol at a particular temperature

(308.15 K) over the entire concentration range investigated. The negative ΔG_A^0 values indicate that the counterion condensation process is spontaneous for the present polyelectrolyte system over the entire concentration range although the process becomes less spontaneous as the concentration increases. Addition of an increasing amount of methanol to the medium makes the counterion condensation process more favourable. Addition of the external salt has, also, been found to increase the spontaneity of counterion condensation.

The Coefficient of Friction between the Polyion and the Solvent (f_{ps}) and its Variation with Polyelectrolyte Concentration, Solvent Medium and Temperature

The friction coefficient provides a measure of the friction between a monomer unit of the polyion and the solvent and can be estimated from the following expression[25]

$$f_{ps} = \frac{|z_p| fF^2}{\lambda_p} \tag{16}$$

where z_p is the number of elementary charges on the monomer unit of the completely dissociated polyion, and the other symbols have their usual significance. The results are summarized in Figs. 12 - 14, which show the dependence of f_{ps} on c in 10, 20, and 30 vol. % methanol-water mixtures at 308.15 K. We can see from the coefficients of friction of the carboxymethylcellulose ion that the possible conformational changes of the molecules caused by dilution lead to change in solvodyanamic resistance. An increase in the friction coefficients with increasing methanol content of the mixture over the entire polyelectrolyte concentration range reflects bigger sizes of the monomer units as the medium becomes richer in the organic cosolvent. An increase in the salt concentration (0.0001 M to 0.01 M) for a particular solvent mixture for sodium chloride and sodium bromide resulted in an increase in the friction coefficients. It has also been seen that addition of sodium bromide lowers the friction coefficient than does the addition of sodium chloride of the same concentration.

Conclusions

An investigation on the electrical conductivity of an anionic polyelectrolyte, sodium carboxymethylcellulose, in methanol-water mixed solvent media containing 10, 20 and 30 vol.% of methanol have been performed in 308.15 K as a function of polymer concentration in presence of added salts (*i.e.*, NaCl , NaBr). The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter developed recently by one of us following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*[9] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[10] Excellent agreement between the experimental results and those obtained following this approach has always been observed. The present experimental results, thus, provide a further support in favor of the validity of this model for the conductivity of polyelectrolyte-salt solutions. The influences of polymer concentration, medium, added salt concentration the fraction of uncondensed counterions, polyion conductance, and other thermodynamic parameters have also been discussed from the viewpoints of polyion-counterion interactions, solvation of counterions and the polyionic sites, and counterion dissociation.

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Table 1. Fractions of Uncondensed Counterions (f') for Sodium Carboxymethylcellulose in Methanol–Water Mixed Solvent Media in presence of Salts following the Scaling Theory Approach using Good Solvent Correlation along with the respective Standard deviations (σ)

Vol.% of Methanol	Salt Conc. (Eqv.L^{-1})	f'	σ
	Sodium Bromide (NaBr)		
10	0.01	0.5102	1.34×10^{-5}
	0.001	0.5714	1.04×10^{-5}
	0.0001	0.5882	6.76×10^{-6}
20	0.01	0.4902	7.23×10^{-6}
	0.001	0.5236	1.24×10^{-5}
	0.0001	0.5435	4.33×10^{-6}
30	0.01	0.4405	6.77×10^{-6}
	0.001	0.5102	5.34×10^{-6}
	0.0001	0.5208	2.22×10^{-6}
	Sodium Chloride (NaCl)		
10	0.01	0.5000	1.46×10^{-5}
	0.001	0.5682	2.13×10^{-5}
	0.0001	0.5747	1.00×10^{-5}
20	0.01	0.4739	1.60×10^{-5}
	0.001	0.5076	9.12×10^{-6}
	0.0001	0.5319	1.07×10^{-5}
30	0.01	0.4348	2.18×10^{-5}
	0.001	0.4695	7.62×10^{-6}
	0.0001	0.4926	4.32×10^{-6}

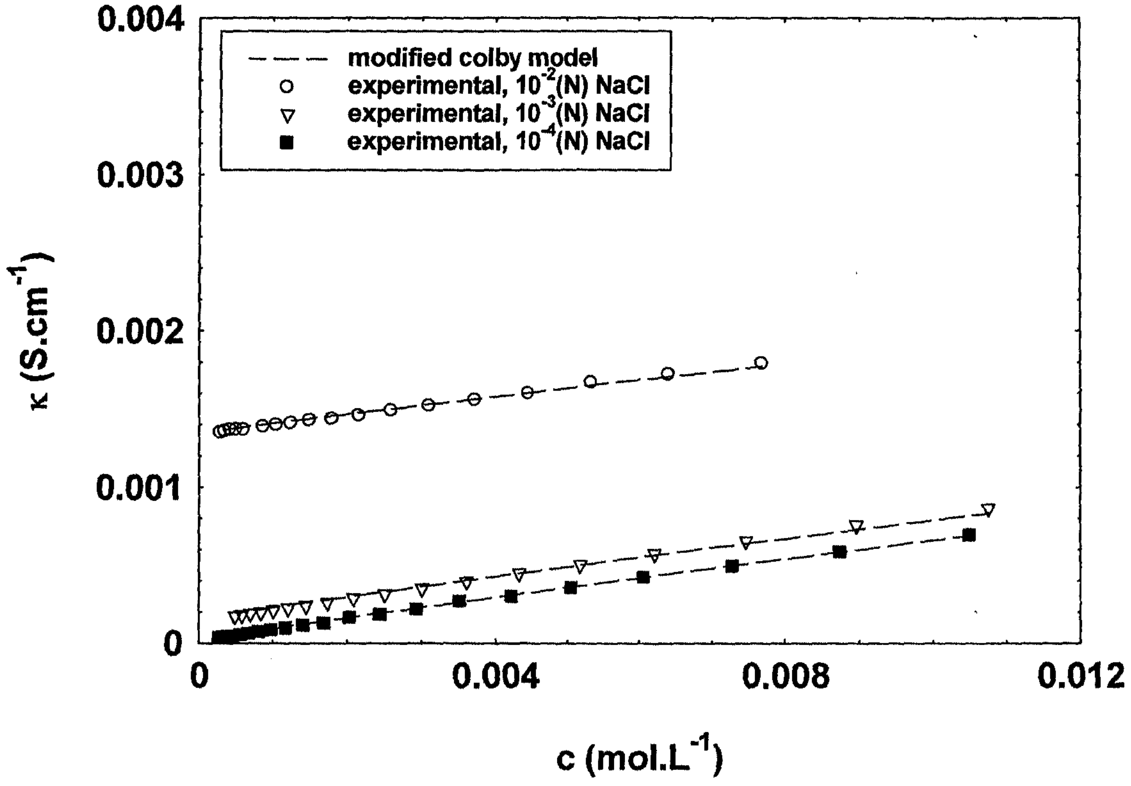

Fig. 1. Variation of the specific conductance (*κ*) of sodium carboxymethylcellulose solution as a function polyelectrolyte concentration in presence of three different added NaCl salt concentration in 10 vol. % methanol-water solvent mixture.

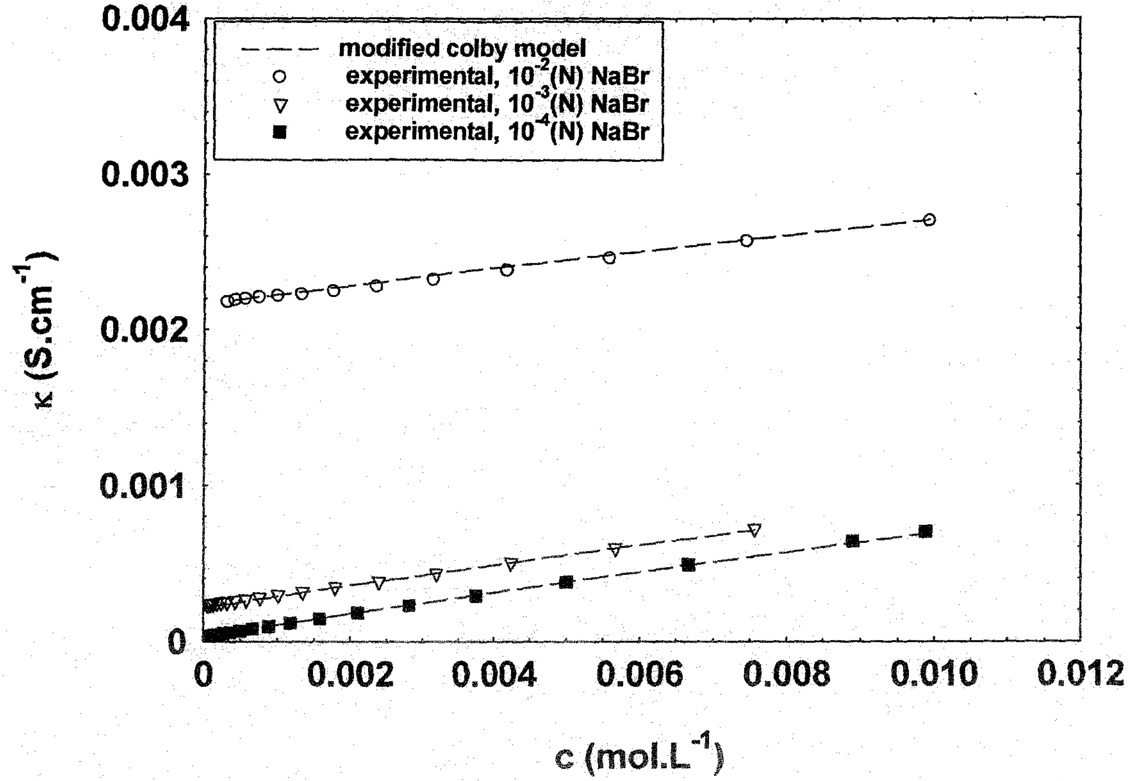

Fig. 2. Variation of the specific conductance (κ) of sodium carboxymethylcellulose solution as a function polyelectrolyte concentration in presence of three different added NaBr salt concentration in 10 vol. % methanol-water solvent mixture.

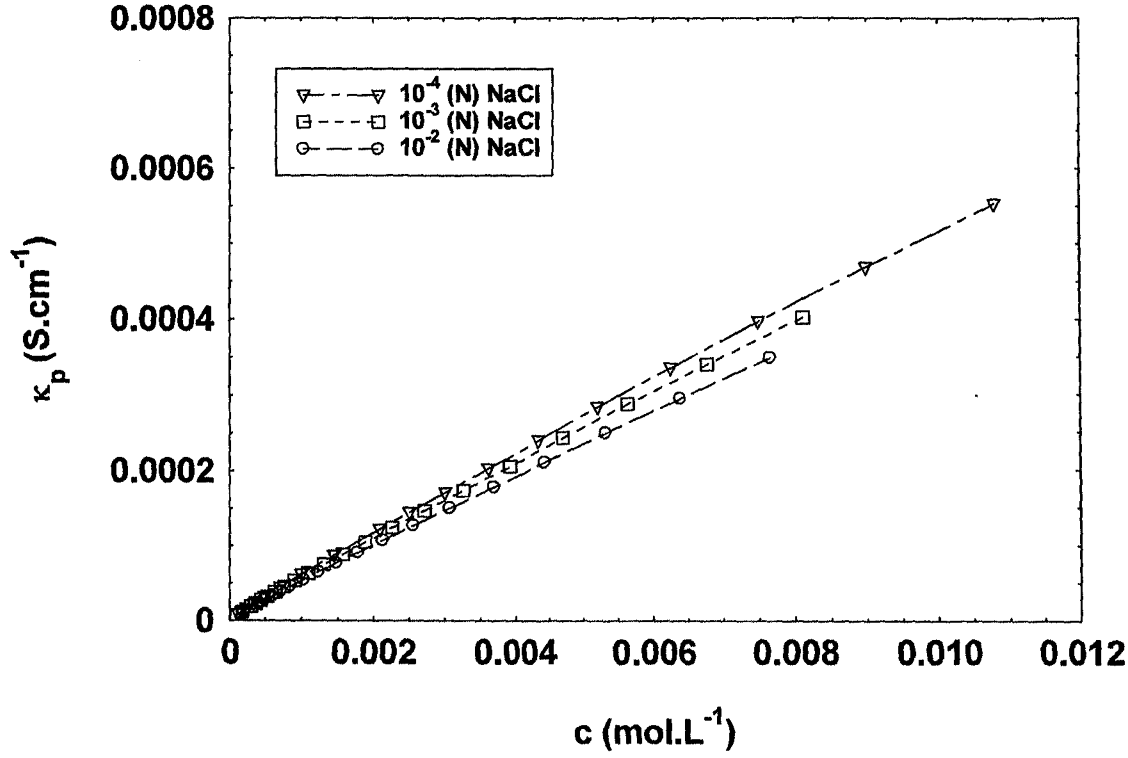

Fig. 3. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

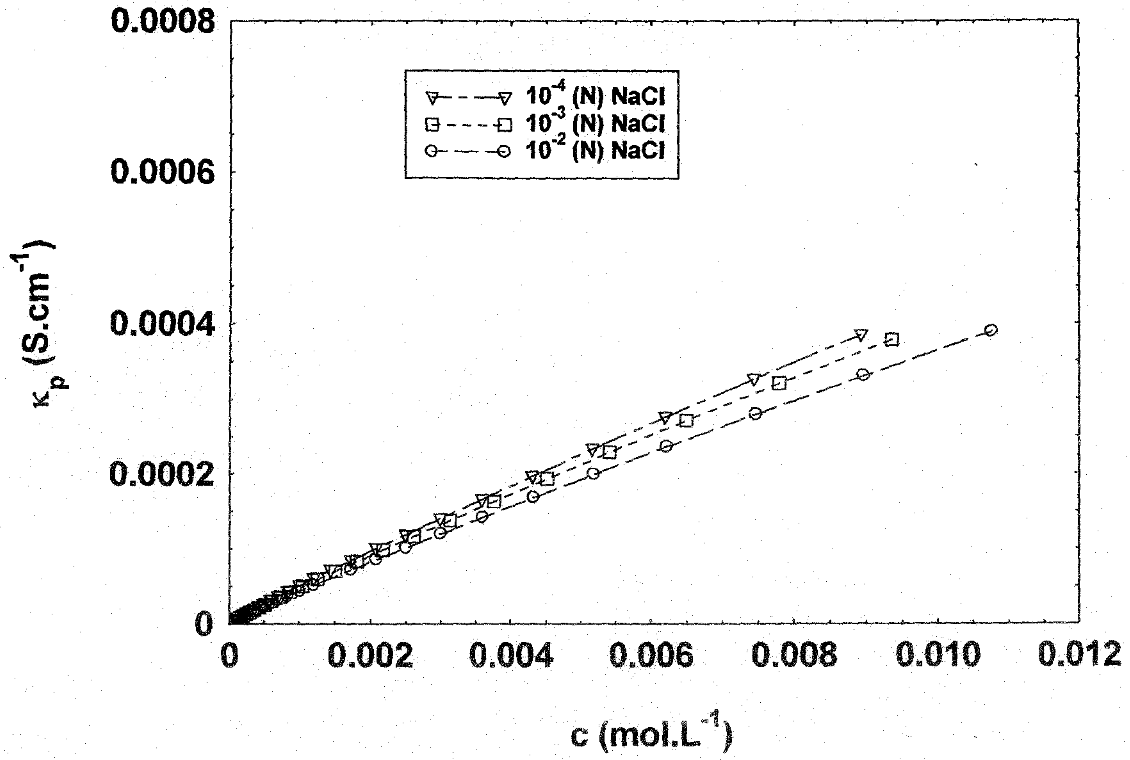

Fig. 4. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 30 vol. % methanol-water mixture.

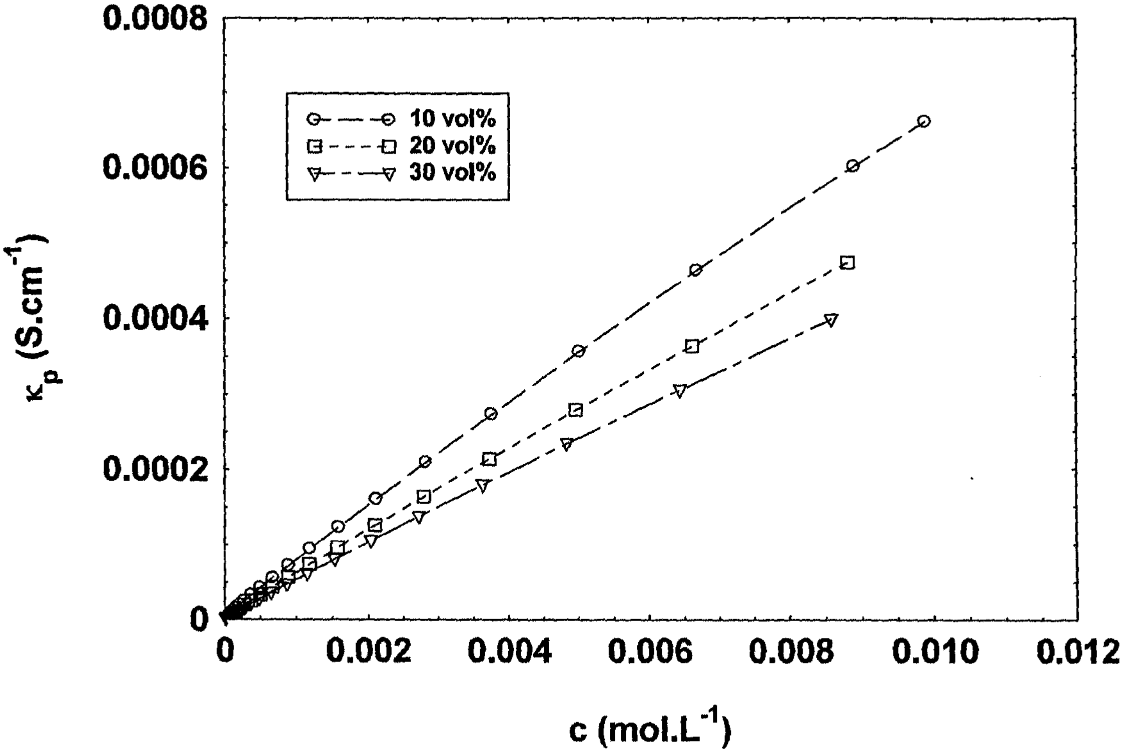

Fig. 5. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added 10^{-4} (N) NaBr salt concentration in different (10, 20, and 30 vol. %) methanol-water mixtures.

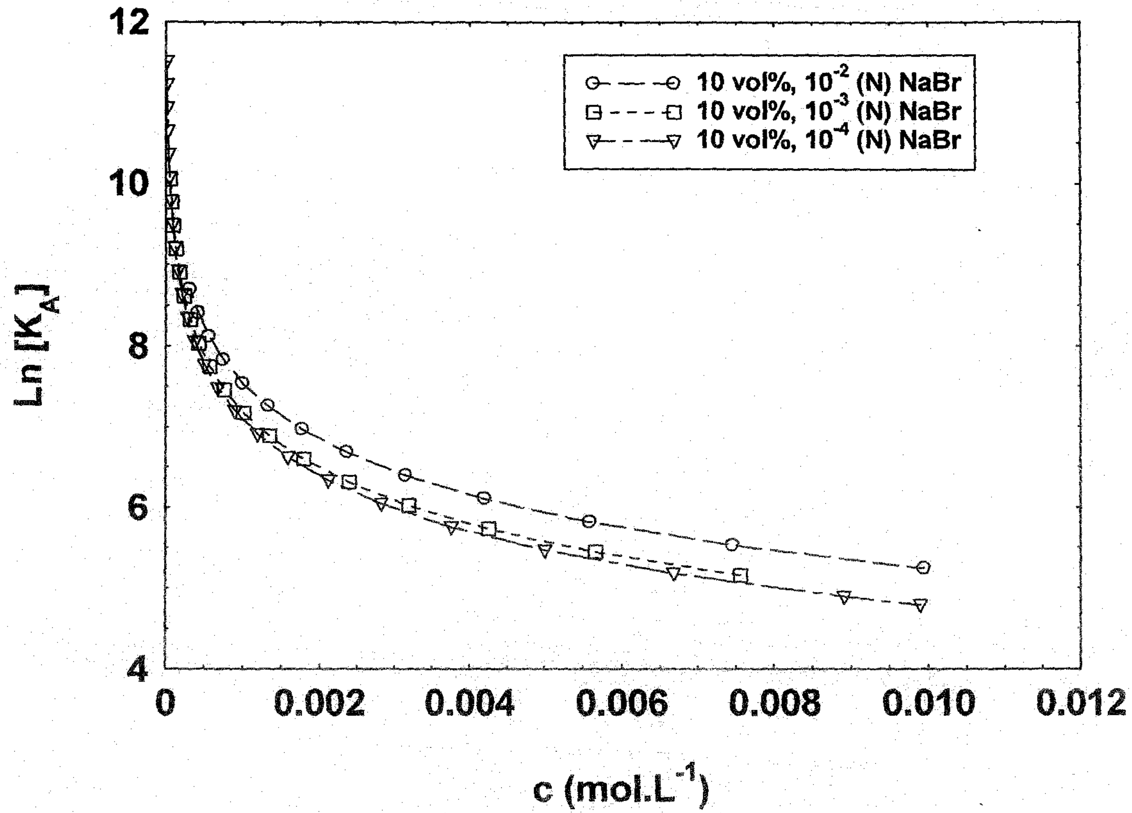

Fig. 6. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of different added NaBr concentration in 10 vol. % methanol-water mixture.

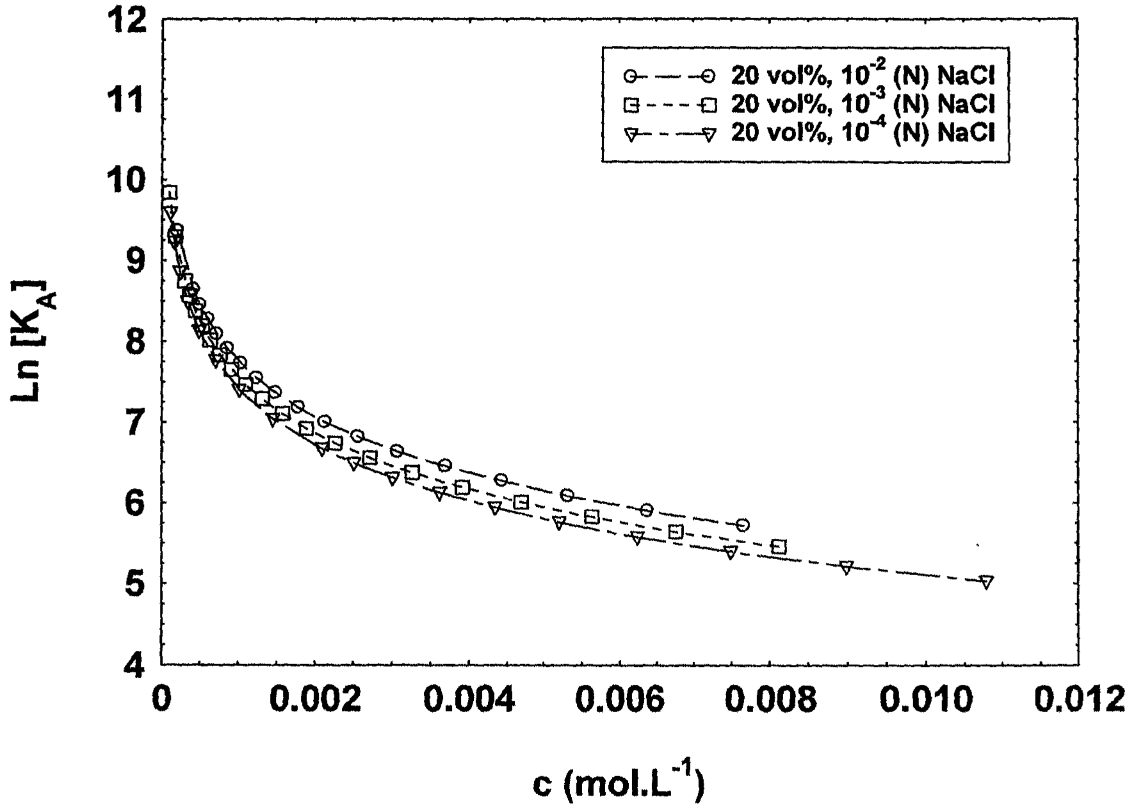

Fig. 7. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

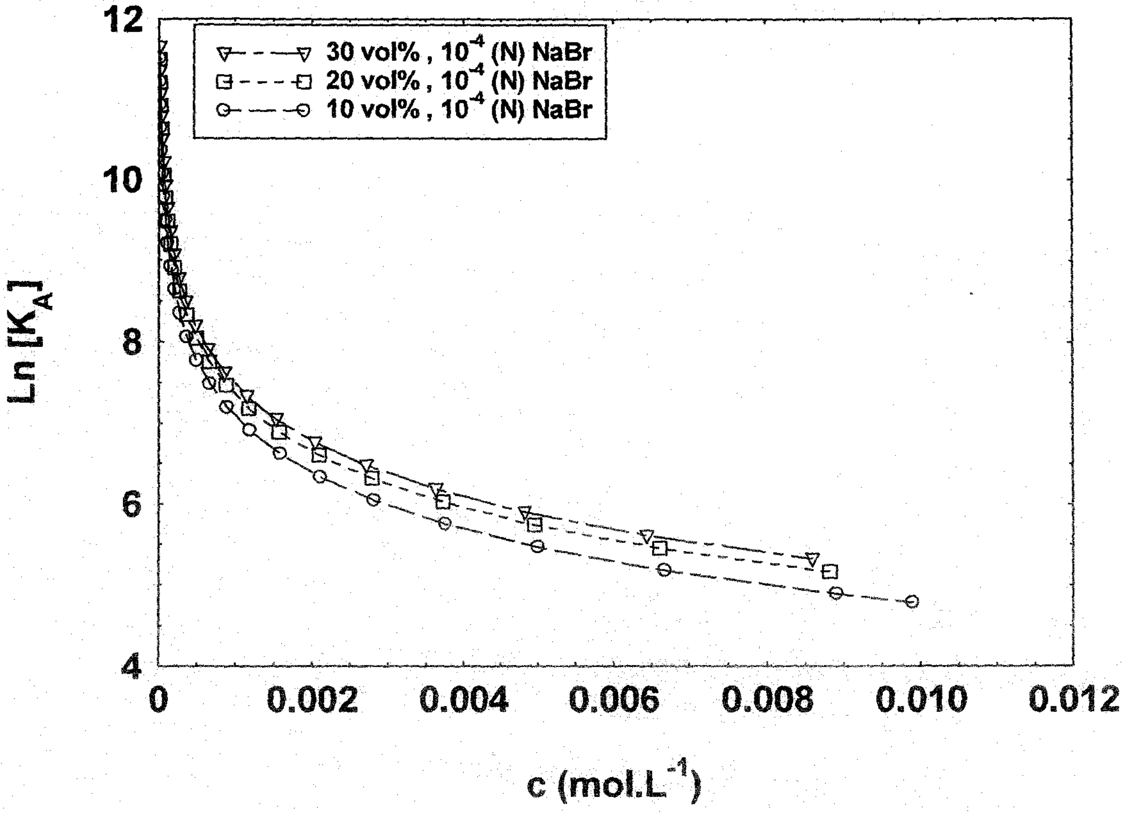

Fig. 8. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of 10^{-4} (N) added NaBr salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.

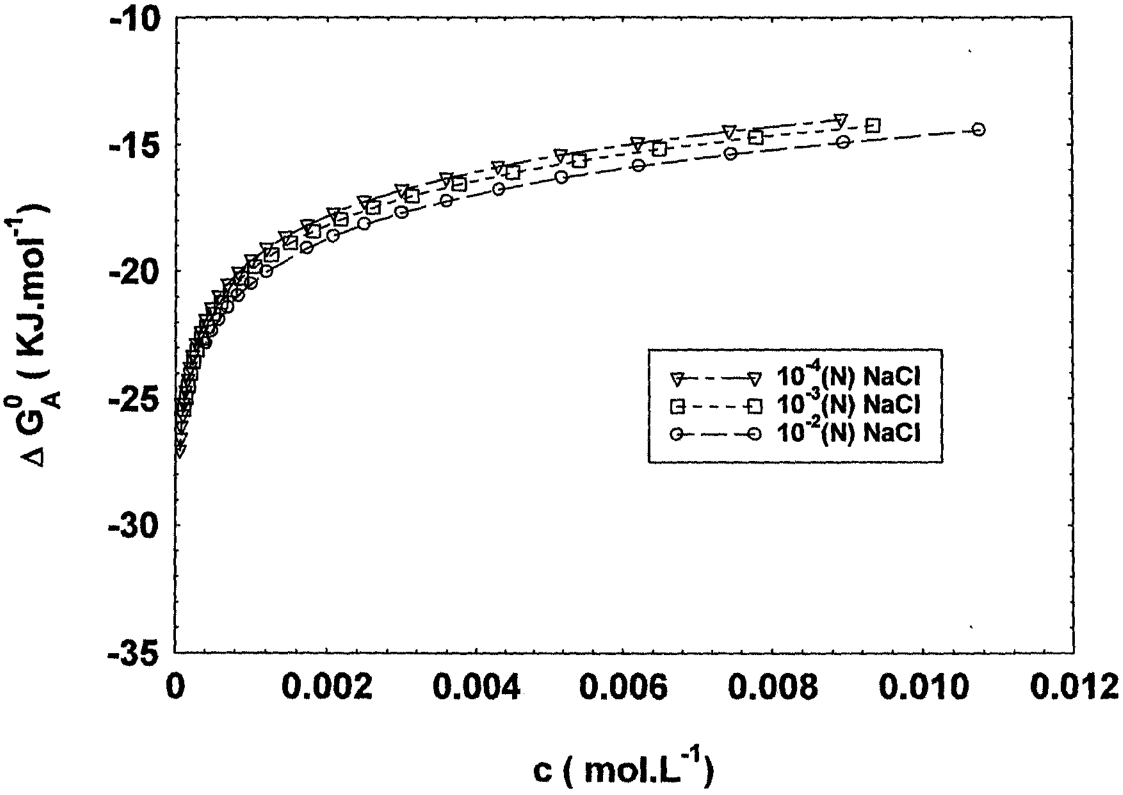

Fig. 9. Variation of standard free energy change of counterion condensation (ΔG_A^0) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added different strength of NaCl salt concentration in 30 vol. % methanol-water mixture.

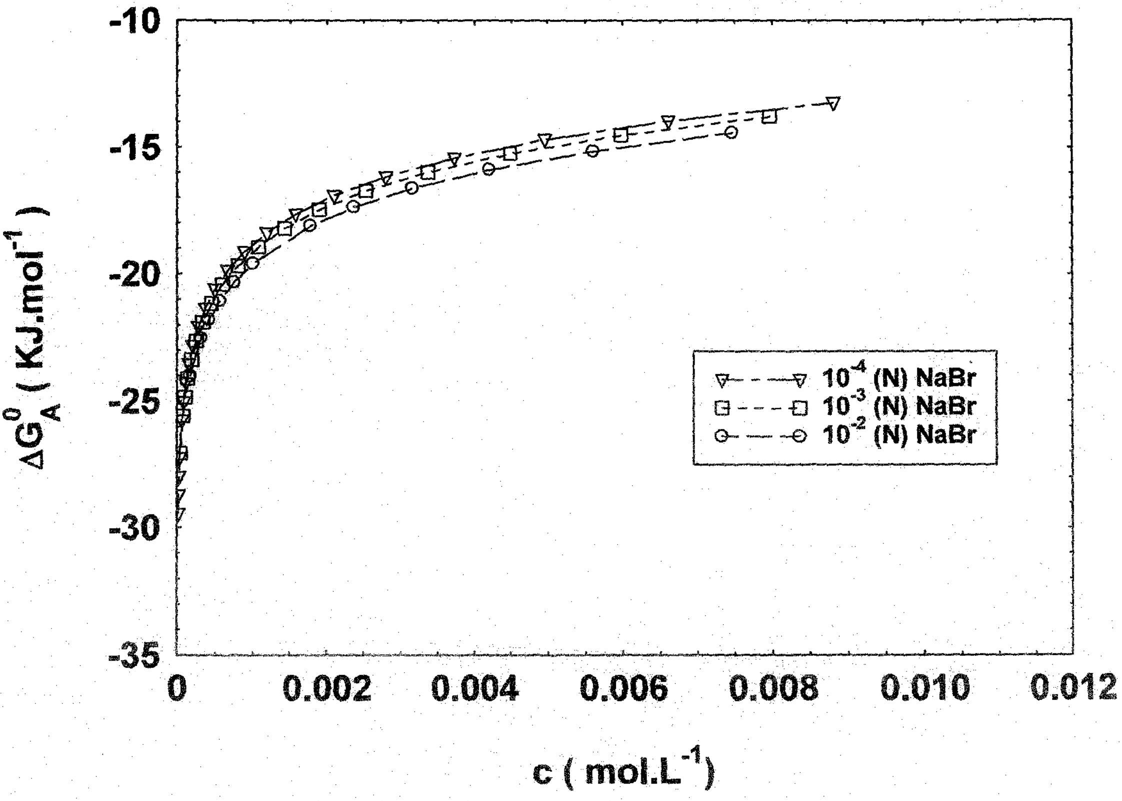

Fig. 10. Variation of standard free energy change of counterion condensation (ΔG_A^0) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added different strength of NaBr salt concentration in 20 vol. % methanol-water mixture.

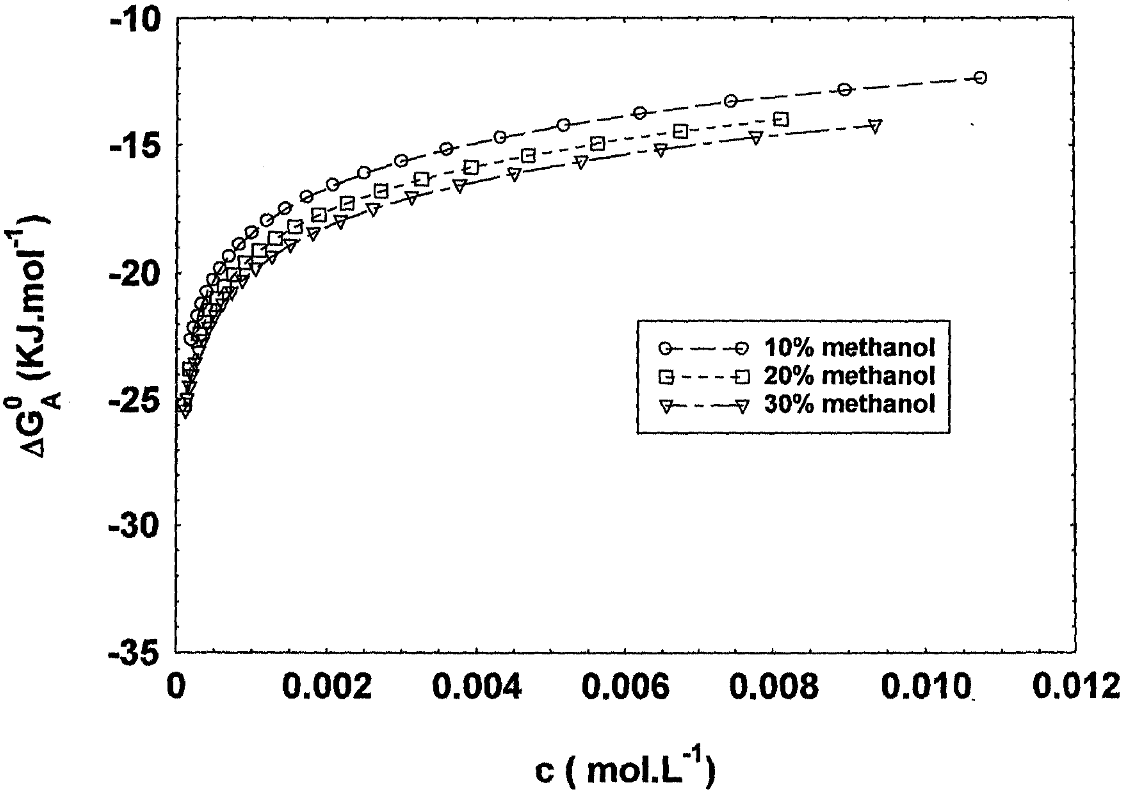

Fig. 11. Variation of standard free energy change of counterion condensation (ΔG^0_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added strength of 10^{-3}(N) NaCl salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.

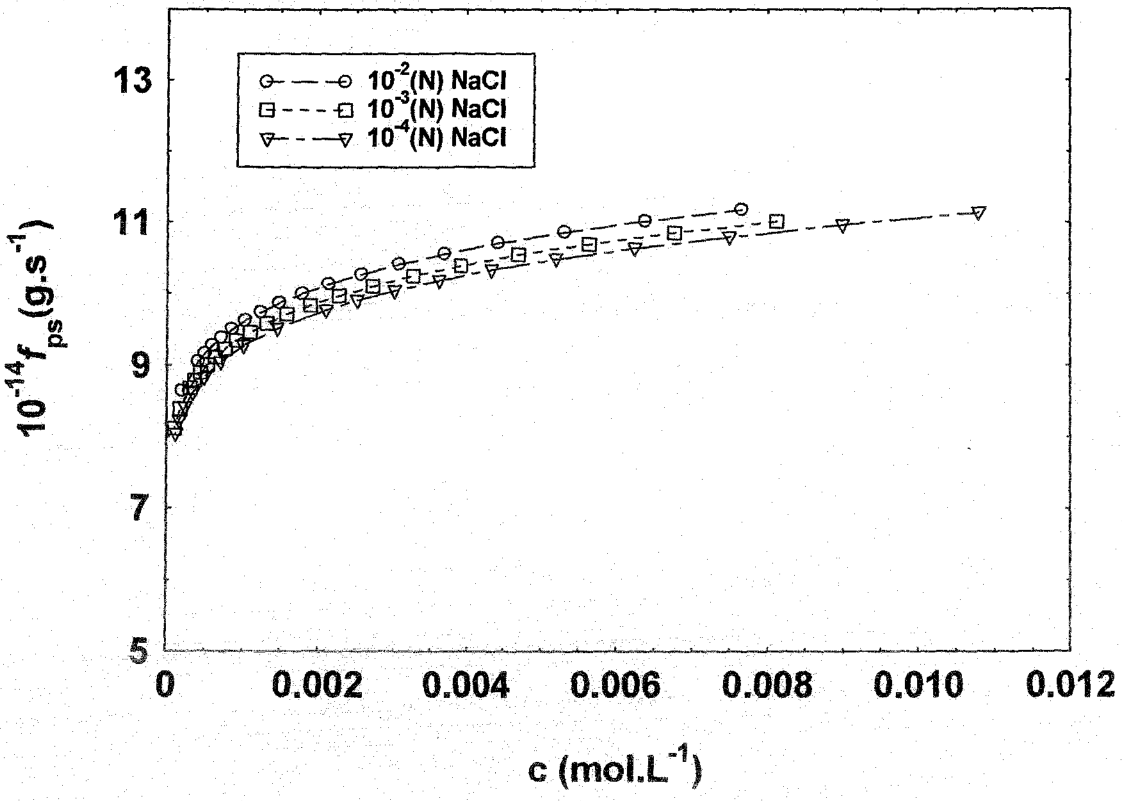

Fig. 12. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

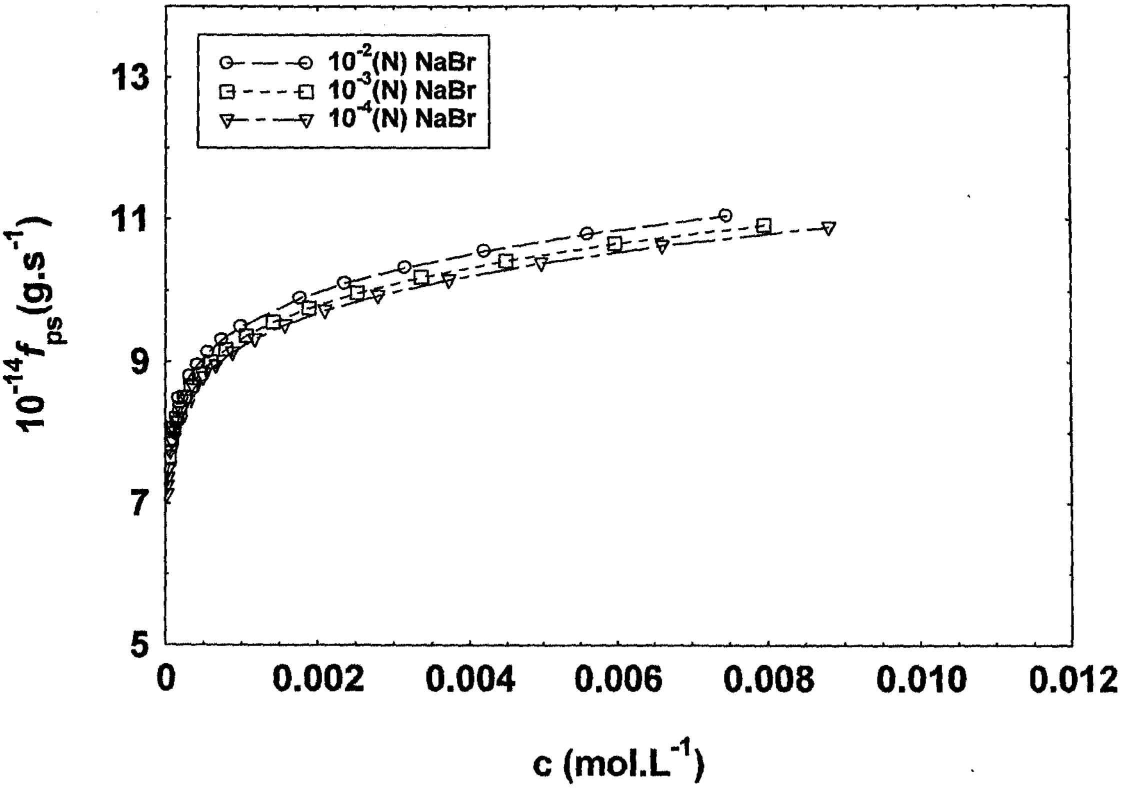

Fig. 13. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaBr salt concentration in 20 vol. % methanol-water mixture.

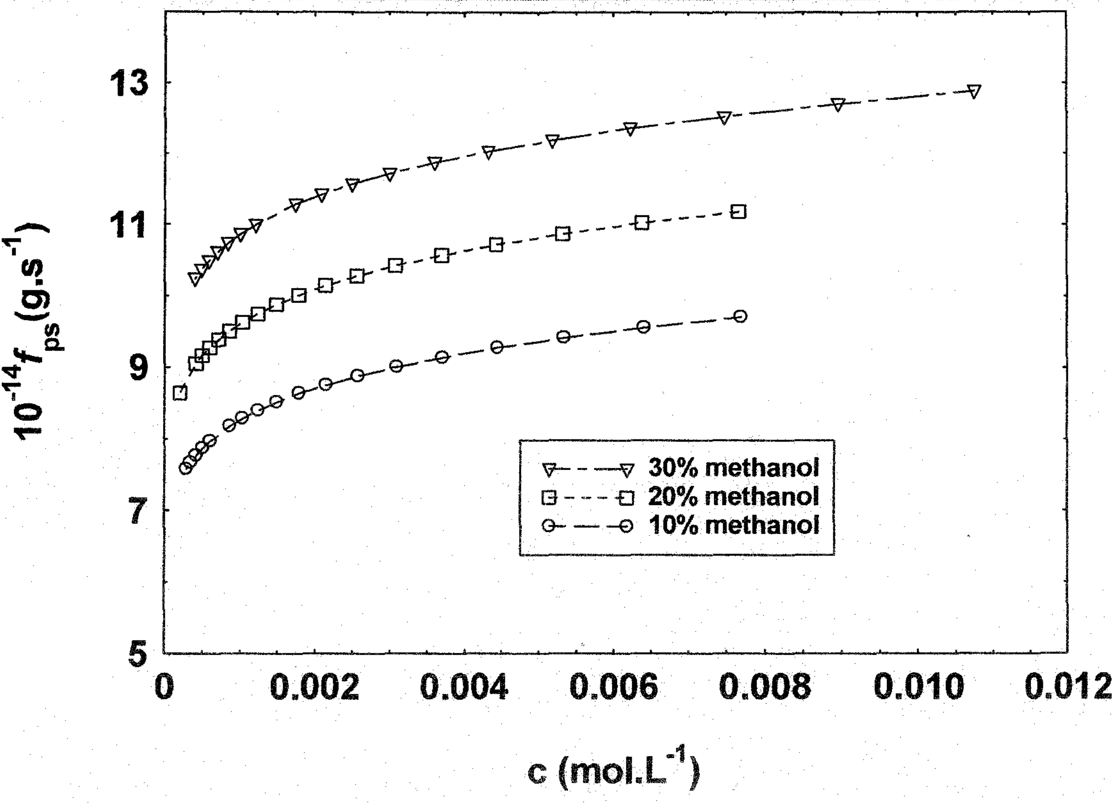

Fig. 14. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of 10^{-2}(N) added NaCl salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.

Chapter 6

Intrinsic Viscosities of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media Using the Isoionic Dilution Method

Introduction

Intrinsic viscosity has always been an important parameter in determining the conformation of a single polymer chain dissolved in solutions.

In case of uncharged polymer solutions, the reduced viscosity (η_{sp}/c ; η_{sp}= specific viscosity and c = polymer concentration) varies linearly with concentration c in dilute solutions which led Huggins to propose the following equation[1,2]

$$\eta_{\mathrm{sp}}/c=[\eta]+k_{\mathrm{H}}[\eta]^2c \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behavior of the polymer molecules in solution and k_{H} is the Huggins constant which is a characteristic for a given polymer-solvent system. This well-known relation has been extensively used for determining the intrinsic viscosity of uncharged polymers simply by extrapolating η_{sp}/c vs. c values to $c=0$.

Due to the presence of electric charges along the polymer chains in polyelectrolytes, the behavior of these species in solutions is entirely different from that of uncharged polymers which are characterized by complex interactions, structures, and dyanamics.[1,3-5] The reduced viscosity of polyelectrolyte solutions, particularly in salt-free and low-added-salt solutions exhibits an anomalous behavior.

Early investigations appeared to suggest a monotonous increase in the reduced viscosity of polyelectrolyte solutions with no-added salt as one lowers the polyion concentration.[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 of polyelectrolyte solutions 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 vs. c profiles results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum, the pair potential attains its maximum value – it decreases upon dilution because of an increase in intermolecular distances and it also decreases with increasing concentration due to the screening of electrostatic interactions. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polyelectrolyte concentration and, therefore, was close to the limit of the accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations below the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

Isoionic dilution[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. 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] Moreover, intrinsic viscosities obtained at different ionic strengths (and hence at different polyelectrolyte concentrations) in conjunction with the reduced viscosities as a function of concentrations of salt-free polyelectrolyte solutions have been shown to provide an opportunity to separate the conformational and electrostatic contributions to the reduced viscosities from experimental results.[13]

The principal objective of the present investigation is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium carboxymethylcellulose in aqueous and methanol-water mixed solvent media. The influences of the medium, and total ionic strength on the intrinsic viscosities and the Huggins constants will be interpreted in terms of the various phenomena occurring in polyelectrolyte solutions. A convenient method has recently been proposed by one of us to decompose the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components *from purely experimental considerations.*[13] A theoretical approach was proposed by Nishida *et al.*[14] for calculating the electrostatic contributions to the reduced viscosity of polyelectrolyte solutions. The investigation made by our group in aqueous ethylene glycol media[13] was the first attempt to separate the intermolecular and intramolecular contributions to reduced viscosity from experimental point of view. The present study carried out in another solvent mixture (methanol-water) using sodium chloride to maintain the ionic strength will thus also be a test of the validity of the model. Results of viscosity measurements in presence of potassium chloride and barium chloride in aqueous solutions have also been included for the purpose of comparison.

Experimental

Methanol (Acros Organics, 99% pure) was distilled twice. The purified solvent had a density of 0.77728 g.cm^{-3} and a coefficient of viscosity of 0.4747 mPa.s at 308.15 K; these values are in good agreement with the literature values.[15,16] Triply distilled water with a specific conductance of less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents.

Sodium carboxymethylcellulose used in these investigations was purchased from Aldrich Chemicals. The average molecular weight (*M*) of the sample was 90,000 with a degree of substitution (*DS*) of 0.70. It was characterized in a similar fashion as described earlier by us.[13] The average molecular weight of the sample was also estimated from the intrinsic viscosity value using the Mark-Houwink equation with the constants obtained from the literature.[17] DS was determined by a conductometric procedure as described by Eyler *et al.*[18] The viscometric measurements were performed at 308.15 K using a Schultz-Immergut-type viscometer[19] 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.[20,21] 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

$$\frac{\eta_{\mathrm{sp}}}{c} = \frac{t - t_0}{t_0}\frac{1}{c} \tag{2}$$

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

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

Results and Discussion

The typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free sodium carboxymethylcellulose solution in water and methanol-water mixtures with 10, and 20 vol. % of methanol at 308.15 K are shown, respectively, in Figs. 1 - 4. In absence of an added salt, the reduced viscosity is found to increase as the polyelectrolyte concentration decreases, for all systems investigated, bending up at low concentrations thus manifesting the typical polyelectrolyte behavior. No maximum was, however, detected in the η_{sp}/c versus c profiles within the concentration range studied here.

Isoionic dilution was proposed to avoid the conformational change of the polyion thus eliminating the anomalous polyelectrolyte behavior and to determine the intrinsic viscosity of solution.[8-13] As we know that the intrinsic viscosity is the parameter which enables characterization of dimension and configuration of polymer, this may play a crucial role in the discussion of polyelectrolyte behavior in dilute solutions.

Isoionic dilution of sodium carboxymethylcellulose solutions have been performed at four different total ionic strengths in water and two methanol-water mixtures containing 10 and 20 vol.% of methanol at 308.15 K with sodium chloride as the added salt. Three different ionic strengths of potassium chloride and barium chloride were investigated in water at the same temperature.

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

From the present experimental η_{sp}/c versus c data, the intrinsic viscosities and the Huggins constants have been determined by the method of least-squares using Eq. (1) and these are displayed in Figs. 8 - 11. The universal trend of decreasing k_H values with increasing ionic strength is observed in all the cases investigated.

The effects of medium on the intrinsic viscosity and the Huggins constant obtained for constant total ionic strengths in the range (0.911 – 4.15) x 10^{-3} eqv.L^{-1} at 308.15 K are shown in the Figs. 5 and 7, respectively. The influences of ionic strength on the intrinsic viscosity and the Huggins constant in water and methanol-water mixtures, on the other hand, are displayed in Figs. 6 and 8 respectively.

From Figs. 5 and 6, it is apparent that the intrinsic viscosities for the present polyelectrolyte system vary with the total ionic strength and the relative permittivity of the medium. This observation, thus, indicates that the investigated polyelectrolyte sodium carboxymethylcellulose differs quite appreciably in its solvodynamic behavior under varying conditions.

For a given value of the total ionic strength, the values of intrinsic viscosities are found to decrease and those of the Huggins constants are found to increase as the medium becomes richer in methanol (*cf.* Figs. 5 and 7, respectively). Similar type of results has also been reported earlier.[12,13,22-24] The variation of the intrinsic viscosity of sodium carboxymethylcellulose with the amount of methanol present in methanol-water mixed solvent media at a fixed total ionic strength could be ascribed to the changed counterion condensation in solution. The relative permittivity of the medium decreases as the medium becomes richer in methanol resulting in stronger electrostatic interactions between the polyion and the counterions. This brings about more and more counterion condensation onto the polyion chain. Consequently, the Coulomb repulsive interactions between the ionized groups on the polyion chain would decrease which reduces the electrostatic persistence length, thus allowing the chain to coil more tightly. The coiling of the polyion chains is manifested by the decreasing intrinsic viscosity values with increasing amount of methanol in the mixed solvent media. Depletion of counterion concentration with decreasing relative permittivity results in a less effective screening between the polyion chains as the medium becomes richer in methanol. An enhanced intermolecular interaction manifested by the increasing values of the Huggins constants with increasing amount of methanol in the mixed media would thus occur.

For each solvent medium, on the other hand, both the intrinsic viscosities and the Huggins constants are found to decrease as the total ionic strength of the solution increases (*cf.* Figs. 6 and 8, respectively).

For different salts it was found that the values of intrinsic viscosity decreased whereas the values of Huggins constant increased in going from sodium carboxymethylcellulose-sodium chloride, sodium carboxymethylcellulose-potassium chloride and sodium carboxymehyl-cellulose-barium chloride systems of equal ionic strengths. As we go from sodium chloride to barium chloride through potassium chloride, the effect of counterion condensation increased due to smaller solvated size and higher charge density of the cations. The greater difference in the intrinsic viscosity values between sodium chloride and barium chloride as compared to that between sodium chloride and potassium chloride clearly indicates that the charge effect may play a vital role in counterion condensation which results in coiling of the macromolecular chains.

As the concentration of the ions in the solution increases, counterion binding onto the polyion chain is enhanced considerably. This causes coiling of the macromolecules which is reflected in a decrease in the intrinsic viscosity of the polyelectrolyte solution. Greater screening with increasing ionic strength also causes reduced intermolecular electrostatic interactions and hence gradually lower values of the Huggins constants as the total ionic strength of the solution increases.

Here, we have decomposed the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components from the experimental results following a method developed earlier by one of us.[13] As pointed out earlier, 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 other words, this means that the intrinsic viscosity obtained for a given ionic strength (and hence for a given concentration) of a salt-free polyelectrolyte solution by the method of isoionic dilution corresponds to its conformational state in salt-free situation and thus could be considered as the conformational contribution to the reduced viscosity $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{conformation}}$.

Now, 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,[25,26] *i.e.*,

$$\eta_{\mathrm{sp}}/c_{\mathrm{P}} = (\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{conformation}} + (\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}} \tag{4}$$

where $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}}$ is the electrostatic contribution to the reduced viscosity. This could easily be understood since when interactions are small, contributions of the cross terms are negligible and hence decoupling of these two contributions is possible..

The electrostatic contribution to the reduced viscosity $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}}$ could, therefore, be readily obtained by subtracting the conformational part from the experimental reduced viscosity at the salt-free polyelectrolyte concentration where the isoionic dilution was performed. We have, thus, been able to quantify the conformational and electrostatic contributions of the reduced viscosity of a polyelectrolyte solution using the isoionic dilution method. The electrostatic reduced viscosity thus computed is shown graphically in Fig. 11 as a function of sodium carboxymethylcellulose concentration in water and methanol-water mixed solvent media. It is directly evident from this figure that the electrostatic contribution to the reduced viscosity decreases sharply with increasing polyelectrolyte concentration (and hence the ionic strength) in a given medium. This also verifies quantitatively the conclusions obtained from the Huggins constants as described above. Moreover, a monotonous growth of the electrostatic part on the addition of methanol to water in the medium at a given polyelectrolyte concentration has been clearly demonstrated in this figure in conformity with our earlier contention derived from Huggins constants (see above). The electrostatic contribution is always found to predominate over the conformational part for the present system.

Conclusions

The present chapter reported precise measurements on the viscosities of the solutions of an anionic polyelectrolyte sodium carboxymethylcellulose in water as well as in methanol–

water mixed solvent media containing 10, and 20 vol. % of methanol at 308.15 K. The intrinsic viscosities and the Huggins constants of the polyelectrolyte solutions were obtained using the Huggins equation through isoionic dilution whereby maintaining the total ionic strengths of the solutions at constant level using sodium chloride, potassium chloride, and barium chloride of equal strength. The influences of medium and the total ionic strength on the intrinsic viscosities have been interpreted in terms of counterion condensation and coiling behaviour in the investigated solutions. The variations of Huggins constants, on the other hand, provided information on the intermolecular interactions. A convenient method has been used to decompose the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components. The electrostatic contributions to the reduced viscosities obtained here purely from experimental considerations quantitatively corroborate the conclusions derived from Huggins constants.

Overall, the results obtained in this work are quite useful for understanding the viscometric behaviour of polyelectrolyte solutions and the experimental values of the electrostatic contributions to the reduced viscosity are found to be consistent with the theoretical calculations presented here.

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Table 1. Intrinsic Viscosities $[\eta]$, Huggins Constants k_H, and the Correlation Coefficients of Fits (as r^2) of Sodium Carboxymethylcellulose in Water and Methanol–Water Mixtures Containing 10 and 20 vol. % of Methanol at the Polyelectrolyte Concentrations where Isoionic Dilution was performed at 308.15 K

Salt	Vol.% of methanol	c_p (Eqv.L^{-1})	$[\eta]$ (L.Eqv^{-1})	k_H	r^2
NaCl	0	9.11×10^{-4}	134	13.42	0.999
		1.25×10^{-3}	130	9.23	0.999
		2.02×10^{-3}	127	4.28	0.996
		4.15×10^{-3}	114	1.78	0.998
	10	9.11×10^{-4}	107	21.05	0.996
		1.25×10^{-3}	104	14.98	0.998
		2.02×10^{-3}	97.7	8.06	0.999
		4.15×10^{-3}	86.8	3.58	0.996
	20	9.11×10^{-4}	80.7	41.00	0.999
		1.25×10^{-3}	77.1	30.45	0.999
		2.02×10^{-3}	73.5	15.94	0.999
		4.15×10^{-3}	64.5	7.60	0.996
KCl	0	9.11×10^{-4}	123	16.79	0.999
		2.02×10^{-3}	118	5.34	0.998
		4.15×10^{-3}	107	2.19	0.999
$BaCl_2$	0	9.11×10^{-4}	62.1	85.57	0.987
		2.02×10^{-3}	54.4	36.16	0.992
		4.15×10^{-3}	39.9	26.19	0.995

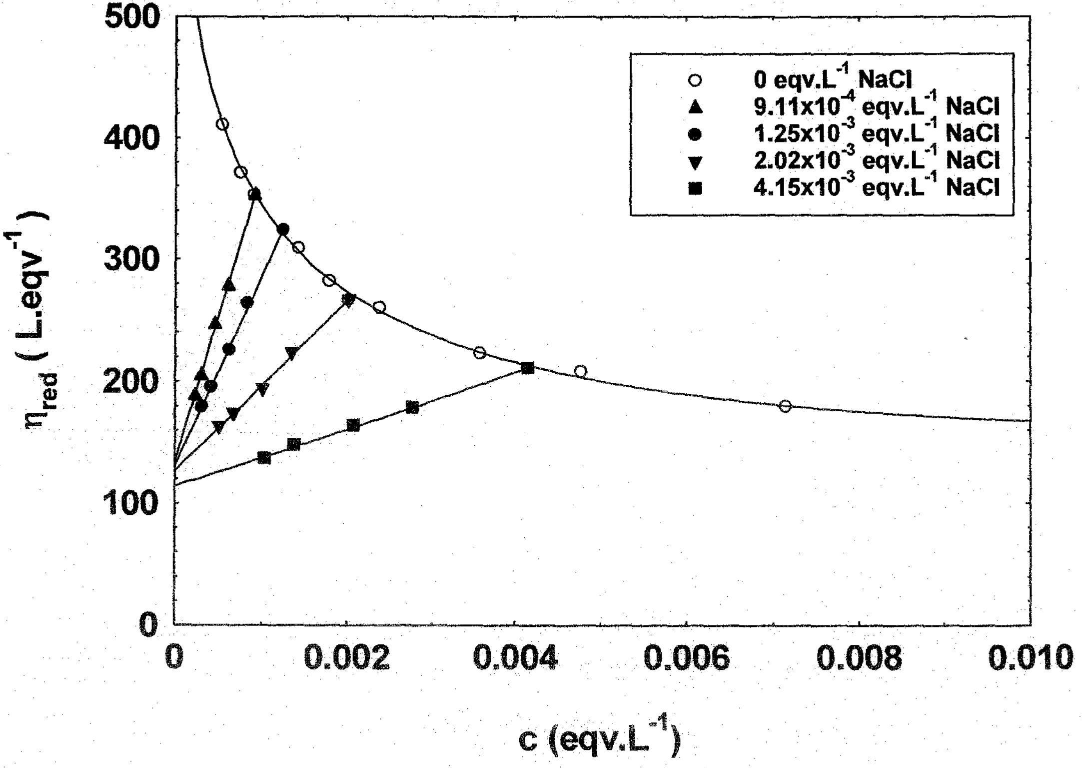

Fig. 1. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using NaCl.

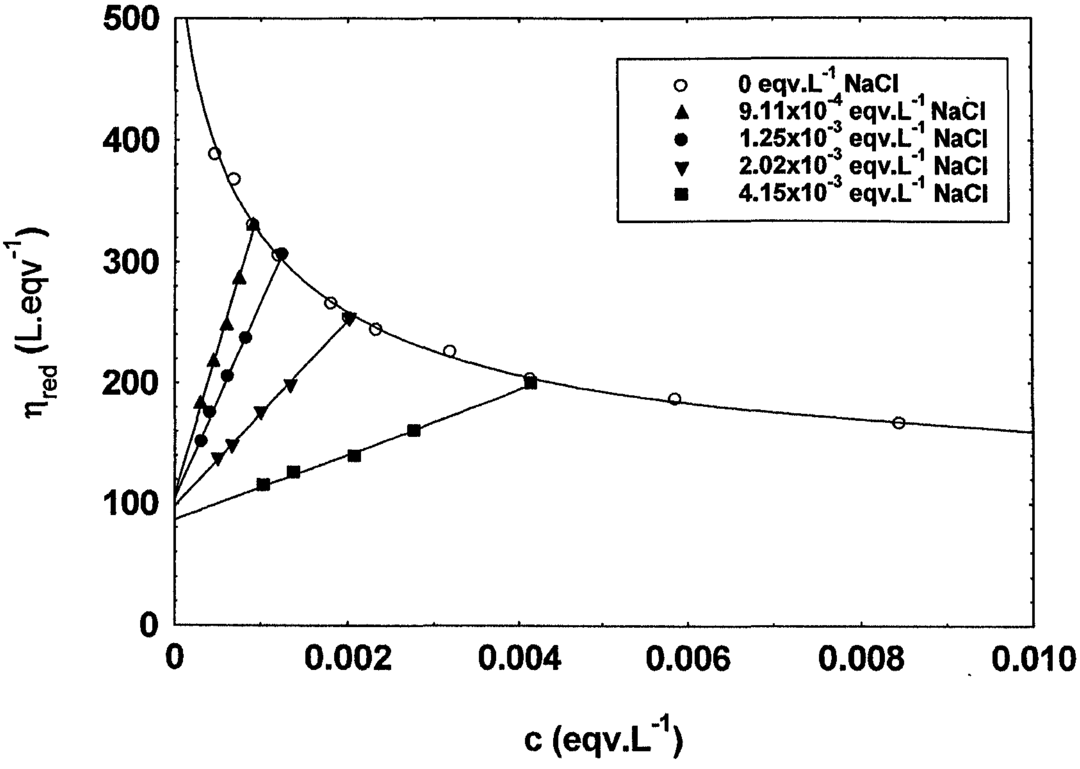

Fig. 2. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in methanol-water mixture containing 10 vol. % of methanol. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using NaCl.

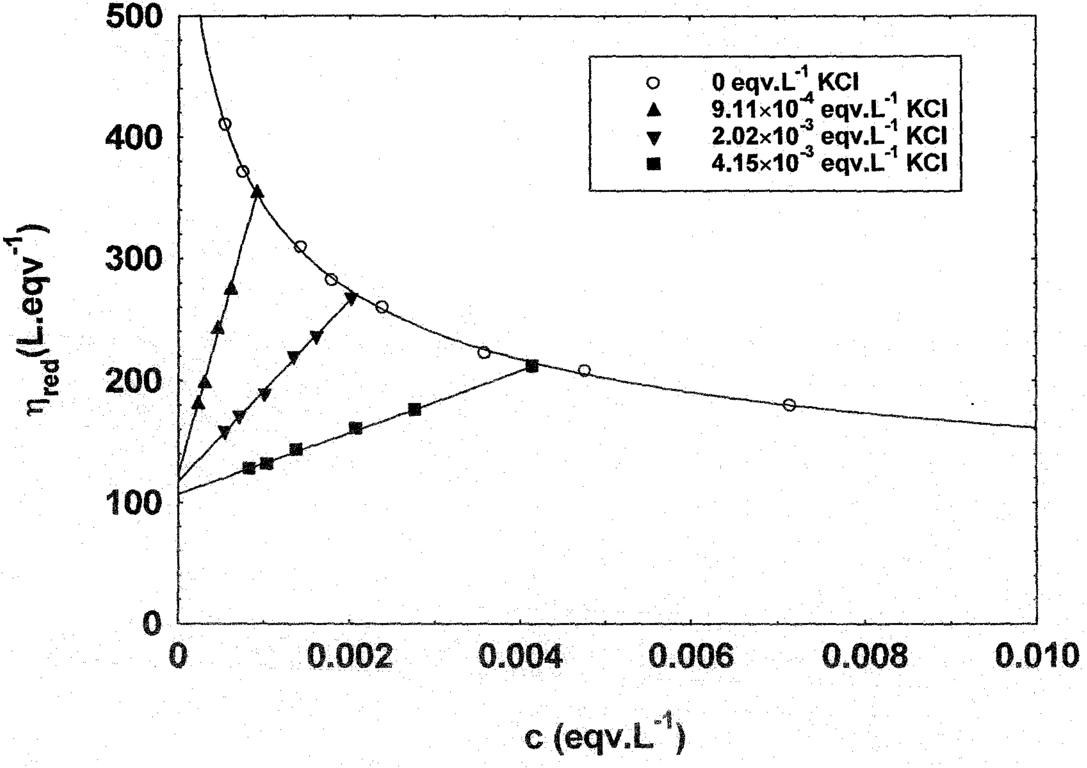

Fig. 3. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using KCl.

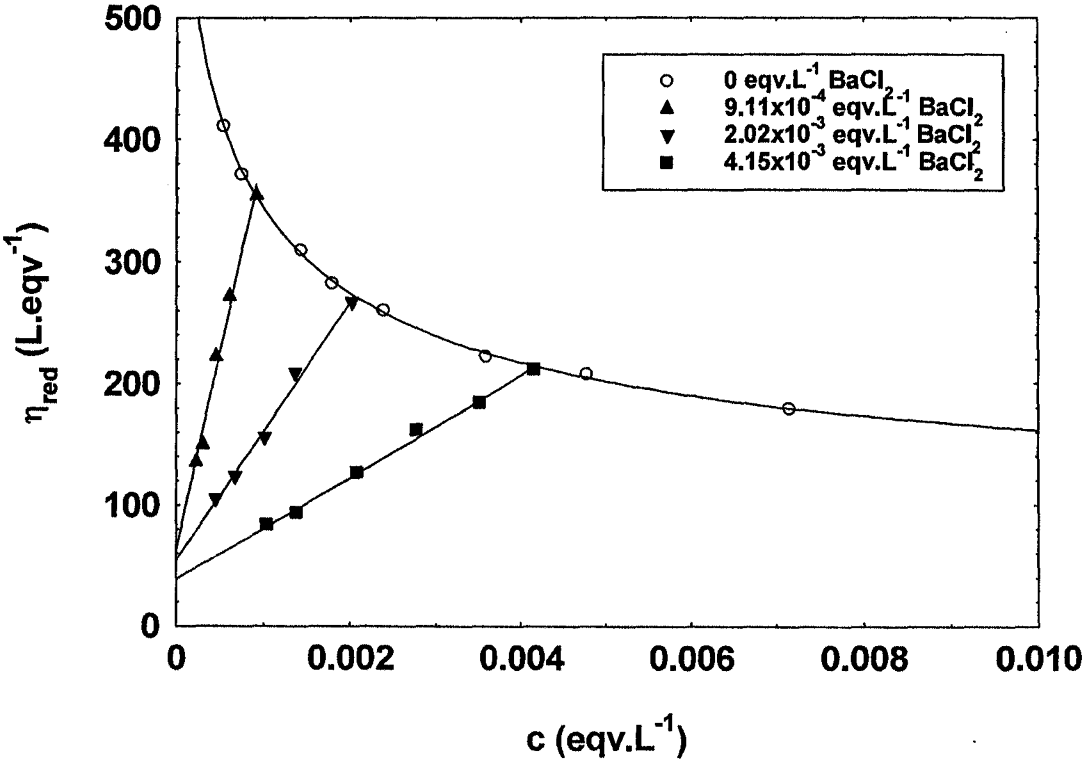

Fig. 4. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at diiferent total ionic strengths where isoionic dilutions were performed by using $BaCl_2$.

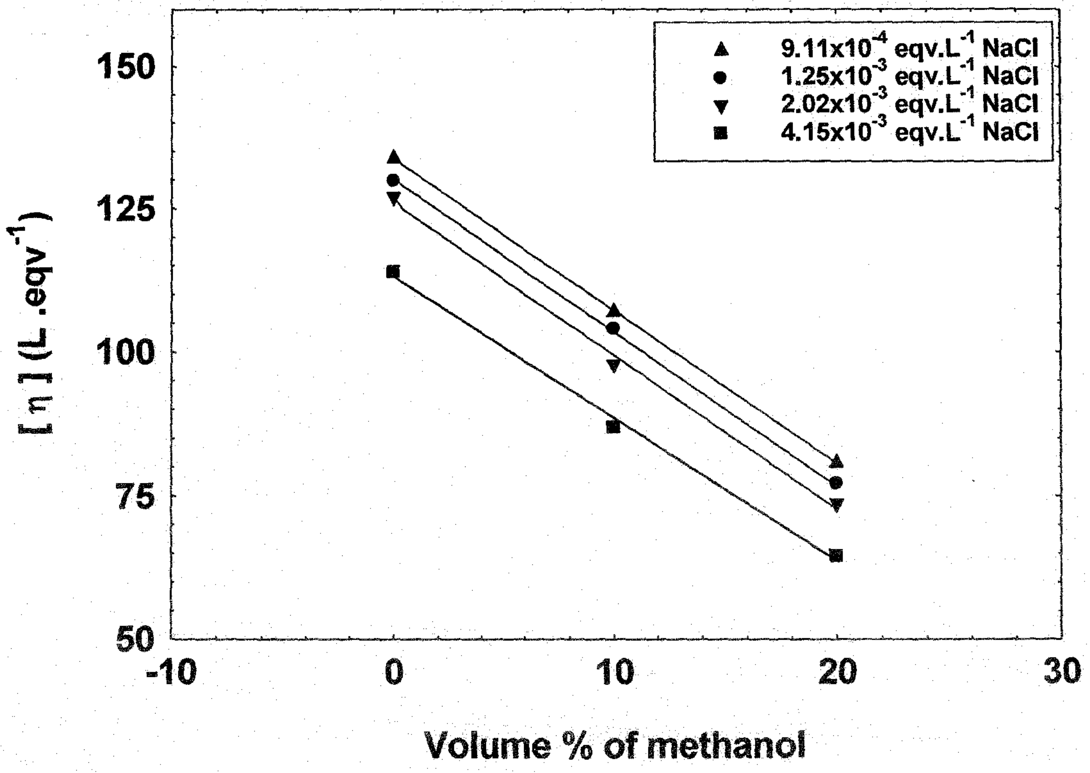

Fig. 5. The effect of medium on the intrinsic viscosity of sodium carboxymethylcellulose in methanol-water mixtures at different total ionic strengths where isoionic dilutions were performed by using NaCl.

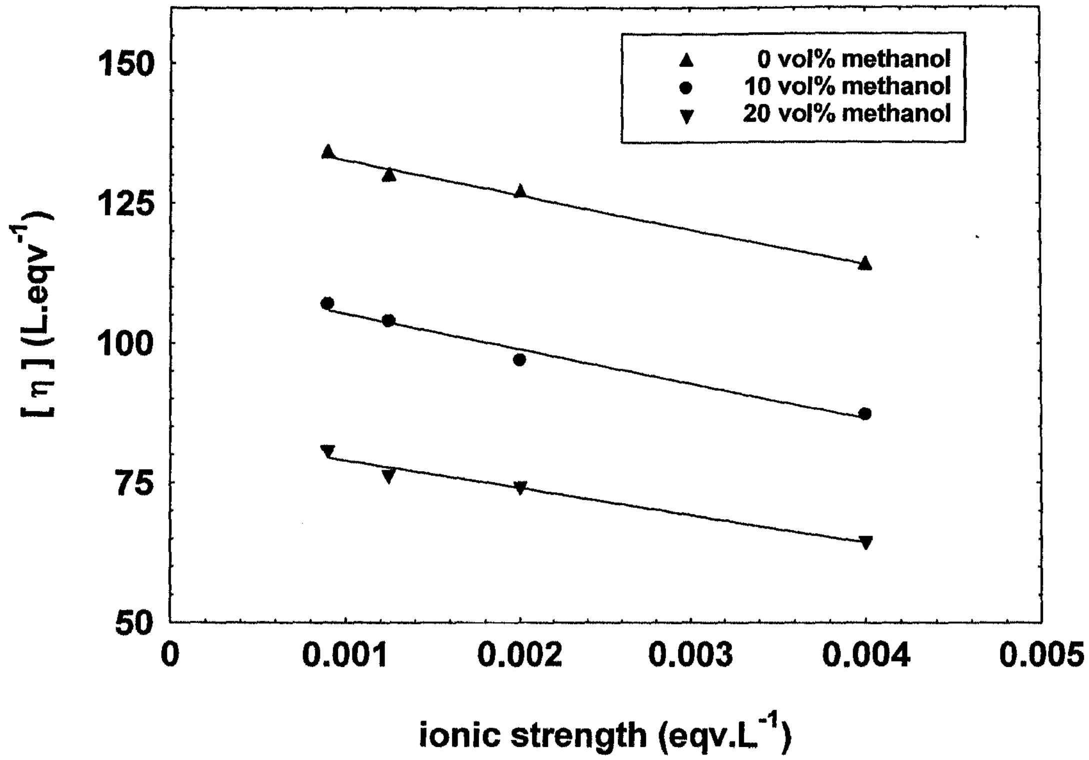

Fig. 6. The effect of total ionic strength on the intrinsic viscosity of sodium carboxymethylcellulose in different methanol-water mixtures, where isoionic dilutions were performed by using NaCl.

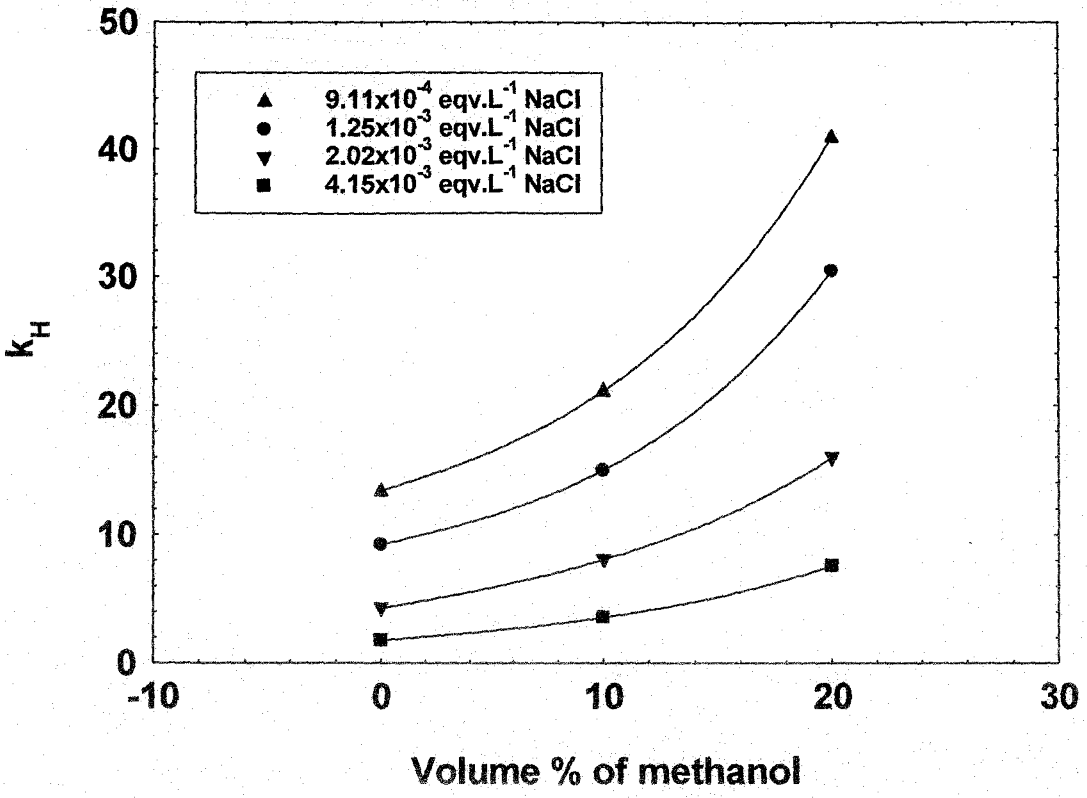

Fig. 7. The effect of medium on the Huggins constant of sodium carboxymethylcellulose in methanol-water mixtures at different total ionic strengths where isoionic dilutions were performed by using NaCl.

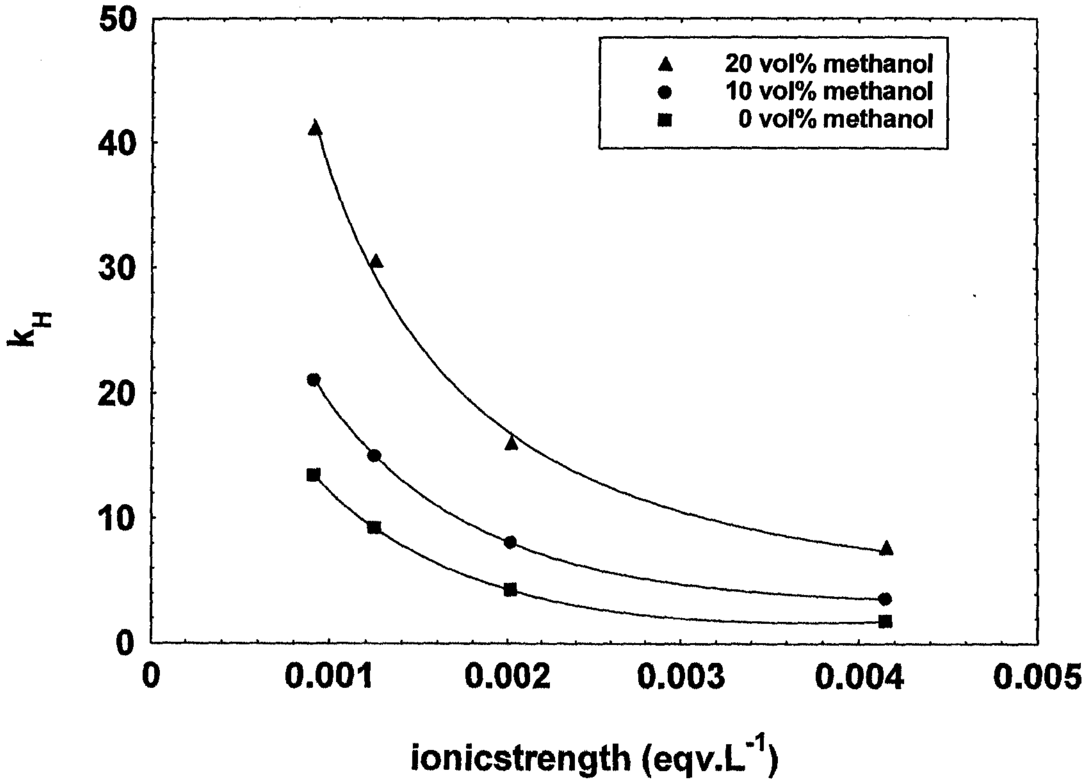

Fig. 8. The effect of total ionic strength on the Huggins constant of sodium carboxymethylcellulose in methanol-water mixtures containing different vol. % of methanol, where isoionic dilutions were performed by using NaCl.

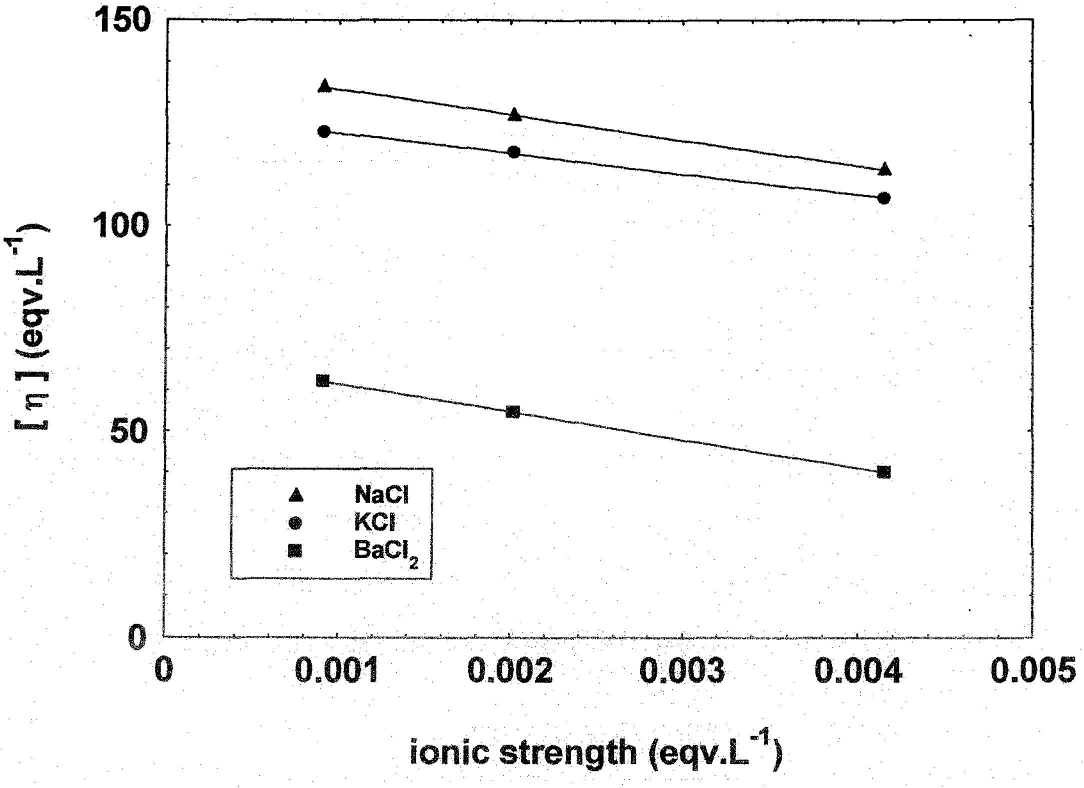

Fig. 9. The effect of different salt on intrinsic viscosity of sodium carboxymethylcellulose by using different salts in water.

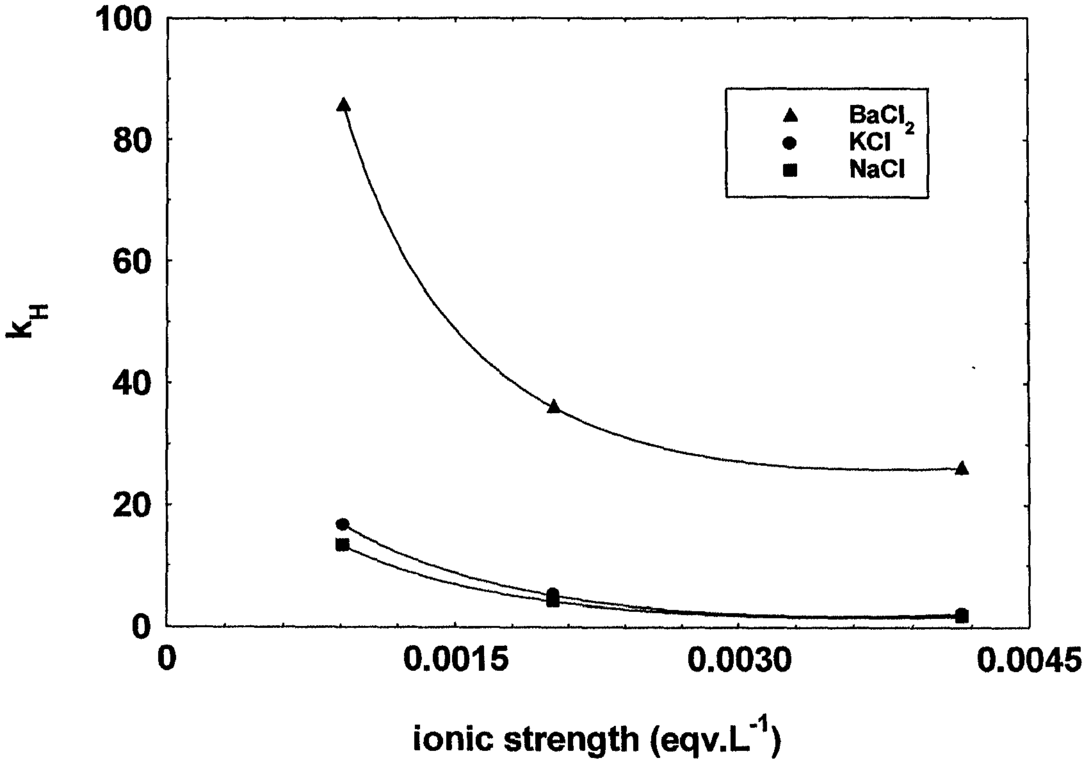

Fig. 10. The effect of different salts on Huggins constant of sodium carboxymethylcellulose by using NaCl, KCl, and $BaCl_2$.

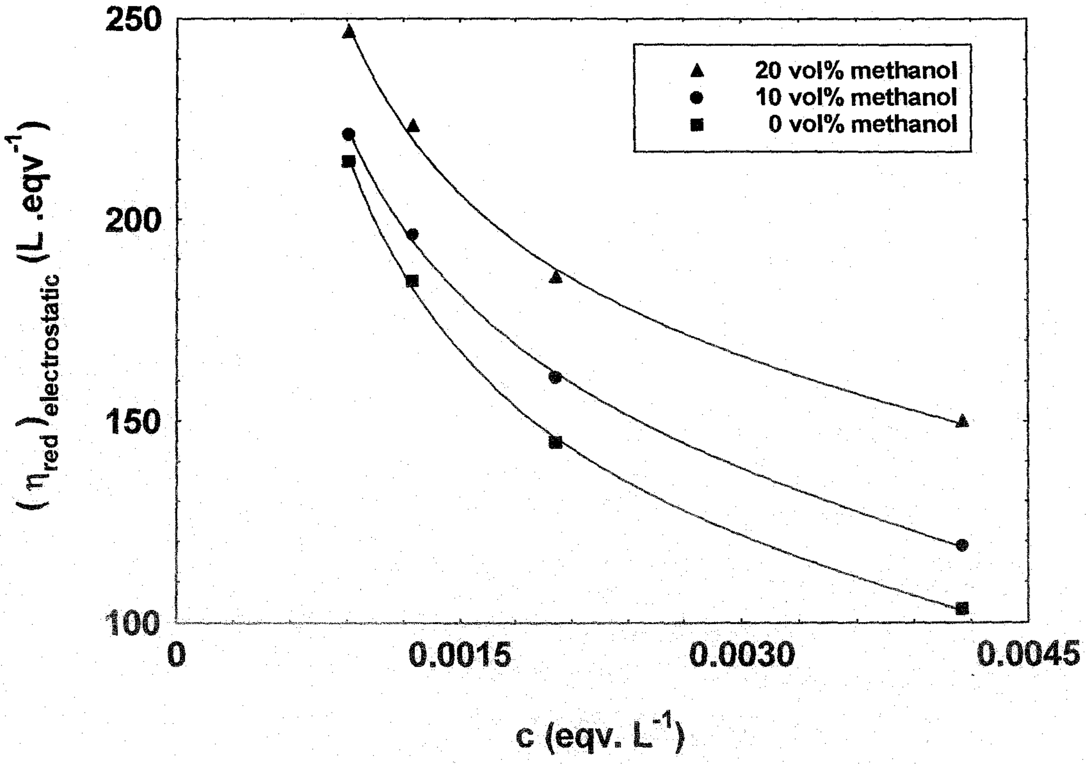

Fig. 11. Electrostatic contribution to the reduced viscosity as a function of polyelectrolyte concentration for sodium carboxymethylcellulose in different methanol-water mixtures.

Chapter 7

Intrinsic Viscosity and Radius of Gyration of Sodium Carboxymethylcellulose in the Absence and in the Presence of a Salt in Aqueous and Mixed Solvent Media

Introduction

A fundamental aspect in understanding the physical properties of a polymer involves determination of the dimension of the macromolecules in a solution. In this context, an accurate determination of the intrinsic viscosity $[\eta]$ and the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ of polymeric samples is of great importance.

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 this distinct polyelectrolyte behavior is 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 to the polymer scientists.

In case of uncharged polymer solutions, the reduced viscosity (η_{sp}/c ; η_{sp}= specific viscosity and c = polymer concentration) varies linearly with concentration c in dilute solutions which led Huggins to propose the following equation[4]:

$$\eta_{\mathrm{sp}}/c = [\eta] + k_{\mathrm{H}}[\eta]^2 c \tag{1}$$

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 vs. c values to

$c = 0$. 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 the reduced viscosity is plotted as a function of the square root of the polyelectrolyte concentration. It was usually assumed that this straight line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero polyelectrolyte 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[6,7] could not be employed to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in the history of polyelectrolyte. It has been argued that the maximum in the η_{sp}/c vs. c profiles results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum, the pair potential attains its maximum value – it decreases upon dilution because of an increase in intermolecular distances and it also decreases with increasing concentration due to the screening of electrostatic interactions. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polyelectrolyte concentration and, therefore, was close to the limit of the accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations below the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

The problem, however, may be solved through screening of the chain charges by addition of an excess of low molar mass electrolytes. Under these circumstances, the values of the intrinsic viscosities depend on the concentration of the added salt. Other attempts to overcome the problem of the determination of the intrinsic viscosities of polyelectrolytes, in particular, under salt-free situations used semiempirical equations.[8-12] Tobitani & Ross-Murphy[13] revisited several models for predicting the polyelectrolyte intrinsic viscosities, and examined their validity by comparison with experiments, and no concurrence on the method which works best was arrived at.

Recently, Wolf presented a purely phenomenological approach to describe quantitatively the variation of the viscosity of polymer solutions as a function of polymer concentration in the range of pair interaction between the polymer coils, and hence to determine the intrinsic viscosities in a very convenient manner.[14] This model has been shown to be equally applicable for charged and uncharged, linear or non-linear macromolecules in salt-free solutions as well as in solutions containing an external low-molecular weight electrolytes.[14-17]

The principal aim of this study is to obtain accurate root-mean-square radii of gyration of a negatively charged polyelectrolyte sodium carboxymethylcellulose in water and methanol-water mixtures both in the absence and in the presence of salt in order to investigate the variation of the solvodynamic behaviour of this polyelectrolyte as a function of the relative permittivity of the medium and of the concentration of the added salt on the basis of a new method developed by us. The method exploits the experimentally determined intrinsic viscosity values obtained as a function of the ionic strength of the medium. Moreover, mixed solvent media provides an excellent opportunity to study the polyion solvodynamic behaviour from a more general point of view since the electrostatic interactions can be modulated conveniently by merely changing the composition of the solvent medium. For this purpose, precise viscosity measurements of the system mentioned above have been performed, and the derived intrinsic viscosity values were translated to the root-mean-square radius of gyration values of the polyion chains.

Cellulose derivatives are carbohydrate polymers which are well-known for their thickening and stabilizing properties, and carboxymethylcelluloses have been considered a "working horse" amongst the anionic polysachharide-based thickeners and stabilizers and find widespread applications in printing pastes and paints, ice creams, cosmetic creams etc.[18] Thus, with an accurate knowledge on their radii of gyration, their solution properties (for example their rheological behavior) and their efficacies in various applications can be predicted.

Theory

Recently, Wolf offered a purely phenomenological approach to depict quantitatively the variation of the viscosity of polymer solutions as a function of polymer concentration.

According to Wolf[14] the concentration dependence of the relative viscosity of a polyelectrolyte in solution can be conveniently expressed as

$$\ln \eta_{\text{rel}} = \frac{c\,[\eta] + Bc^2[\eta][\eta]^*}{1 + Bc\,[\eta]} \tag{2}$$

where B and $[\eta]^*$ are two system-specific constants. The values of the parameters $[\eta]$, B and $[\eta]^*$ can be easily determined on a personal computer from a sufficiently large number of viscosity measurements at different polymer concentrations by any non-linear least-squares fitting program.

Principal features of the connection between the intrinsic viscosity and the coil dimension of *random flight* polymer chains are well established.[19] Thus when the coil dimensions are described in terms of the unperturbed root-mean-square separation of the chain ends $\langle r^2\rangle_\theta^{1/2}$, the intrinsic viscosity in Flory θ solvent media is given by

$$[\eta]_\theta = \Phi_0 \left[\frac{\langle r^2\rangle_\theta}{M}\right]^{3/2} M^{1/2} \tag{3}$$

where Φ_0 is a universal Flory constant[20] and for linear flexible chain molecules under theta conditions is equal to 2.87 x 10^{23} when intrinsic viscosities are expressed in cm^3/g.

The root-mean-square radius of gyration under theta conditions $\langle S^2\rangle_\theta^{1/2}$ can be obtained from the following relationship:

$$[\eta]_\theta = 6^{3/2}\Phi_0 \left[\frac{\langle S^2\rangle_\theta}{M}\right]^{3/2} M^{1/2} \tag{4}$$

To connect chain dimensions and intrinsic viscosities in good solvents the uniform expansion approximation of Flory and Fox[21] is frequently employed whereby it is assumed that the intrinsic viscosity increases in proportion to the cube of the expansion factor α_η for the intrinsic viscosity defined by Reed *et al.*,[22]

$$[\eta]=[\eta]_\theta \alpha_\eta^3 \tag{5}$$

The expansion factor α_η for the intrinsic viscosity is a complex function of the expansion factor for the root-mean-square radius of gyration α_S. Weill and Cloizeaux[23] derived a the following semiempirical relation between α_η and α_S:

$$\alpha_\eta^3 = \alpha_S^{2.43} \tag{6}$$

A knowledge of the expansion factor for the root-mean-square radius of gyration α_S in conjunction with the information on the root-mean-square radius of gyration under theta conditions $\langle S^2\rangle_\theta^{1/2}$ would help ascertain the root-mean-square radius of gyration values under non-θ conditions according to the following relationship:

$$\langle S^2\rangle^{1/2} = \alpha_S \langle S^2\rangle_\theta^{1/2} \tag{7}$$

The $\langle S^2\rangle^{1/2}$ values provide a measure of the actual state of coiling of the polyion chains in experimental solutions.

Experimental

Materials

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance of less than 10^{-6} S/cm at 308.15 K was used for the preparation of the solvent mixtures. Sodium carboxymethylcellulose, a negatively charged polyelectrolyte, employed in this investigation was purchased from Aldrich Chemical Company, Inc. Three samples with average molecular weights (*M*) of 90,000, 250,000, and 700,000 were used; the first sample had a degree of substitution of 0.70, whereas the later two samples had a degree of substitution of 0.90. These were characterized as described earlier by us.[24]

Viscosity Measurements

The viscosity measurements were performed at the experimental temperature using a Schultz-Immergut-type viscometer[25] with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The flow time measurements were carried out in a water 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.[26,27] Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosity values depend on the shear rate within the concentration range investigated, measurements with capillaries of different inner diameters were made. This did not lead to different values of the reduced viscosity.

The reduced viscosity is obtained from

$$\frac{\eta_{sp}}{c} = \frac{t-t_0}{t_0}\frac{1}{c} \tag{8}$$

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

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

Results and Discussion

The representative plots (Figs. 1a – 1c) show the concentration dependence of η_{sp}/c for the sodium carboxymethylcellulose samples investigated in methanol-water mixture containing 30 volume percent of methanol at 308.15 K. For the sample with a molecular weight of 90,000 no maxima in the η_{sp}/c vs. c profiles were detected even in salt-free and the lowest-salt solutions (Fig. 1a); rather appreciable increase in the η_{sp}/c values as the polyelectrolyte concentration decreases was noticed. The 250,000 sample, on the other hand, exhibits maxima in salt-free and the lowest-salt solutions (Fig. 1b). For the sample with the highest molecular weight (700,000) the η_{sp}/c values decrease with the decrease in the polyelectrolyte concentration without manifesting any maxima in salt-free and the lowest-salt solutions (Fig. 1c). It is, thus, apparent that for the 700,000 sample the maxima may be located at the higher concentration region, and we are on the lower concentration side of these maxima. For the 90,000 sample, we are yet to reach the maxima which are expected to appear at even lower polyelectrolyte concentrations. The investigated concentration range is, however, appropriate to manifest the maxima for the 250,000 sample. Thus the position of the maximum in our experiments significantly depends on the molecular weight and is shifted towards smaller polyelectrolyte concentration for smaller polyelectrolyte chains. We also observed similar behavior in the other media investigated. These observations are in good agreement with earlier observations for other aqueous polyelectrolyte systems.[28,29]

The non-linear dependence of η_{sp}/c on polymer concentration - especially in salt-free and low-salt solutions - renders the determination of the intrinsic viscosities for the systems described above using the Huggins relation [Eq. (1)] impossible. Similar difficulties were also encountered with the other systems investigated.

We, therefore, analyzed the primary viscosity data on the basis of the Wolf[15] phenomenological approach [Eq. (2)]. The values of the parameters $[\eta]$, B and $[\eta]^*$ obtained from non-linear least-squares fit of the experimentally determined $\ln\eta_r$ *vs.* c values have been listed in Table 1. Figs. 2a - 2c show the fits in accordance with Eq. (2) by means of the parameters listed in Table 1 along with the experimental results for the sodium carboxymethylcellulose samples investigated in methanol-water mixture containing 30 volume percent of methanol at 308.15 K. An excellent agreement between the experimental and the fitted values demonstrates clearly the efficacy of the Wolf approach for the determination of the intrinsic viscosities.

The experimental $[\eta]$ values show a linear dependence on $c_s^{-1/2}$ (where c_s is the concentration of the added salt) for $c_s \geq 0.001$ mol.L^{-1} for all the systems under investigation (Fig. 3). This kind of linearity of the $[\eta]$ *vs.* $c_s^{-1/2}$ profiles above a certain system-dependent critical salt concentration was also reported earlier for solutions of other polyelectrolytes.[30-33]

We extrapolated the linear plots obtained in the present study to infinite salt concentration in order to determine the limiting values of the intrinsic viscosities. It is interesting to note that these limiting intrinsic viscosity values correspond to the unperturbed conditions (or θ conditions) in an appropriate mixed solvent medium for sodium carboxymethylcellulose samples. These $[\eta]_\theta$ values have, then, been converted into the unperturbed root-mean-square radii of gyration $\langle S^2 \rangle_\theta^{1/2}$ using Eq. (4). Under this condition, the expansion factor α_S will be equal to unity. The $\langle S^2 \rangle_\theta^{1/2}$ values thus obtained are listed in Table 2. These values are also shown graphically in Fig. 4. It is interesting to note that $\langle S^2 \rangle_\theta^{1/2}$ values decreases linearly with the percentage of methanol in the methanol-water media for the three polyelectrolyte samples investigated.

Under non-θ conditions, the polyion chains will expand from their unperturbed values $\langle S^2 \rangle_\theta^{1/2}$. The values of the expansion factors for the radiii of gyration α_S have been estimated from the experimental $[\eta]$ values, and the $[\eta]_\theta$ values (see above) using Eqs. (5) and (6).

We then obtained the radii of gyration values of the polyion chains in salt-free solutions as well as in solutions with finite amount of salt with the aid of Eq. (7). These are recorded in Table 3.

From Table 3, it is apparent that the root-mean-square radii of gyration for the polyelectrolyte systems under investigation vary with the medium at a given ionic strength, and with the ionic strength in a given medium. The effect of added salt is, however, found to be more prominent compared to that of the medium for all the systems. This observation, thus, indicates that the polyelectrolyte sodium carboxymethylcellulose differs appreciably in its solvodynamic behaviour, in particular, when the medium ionic strength is altered. This observed behaviour is consistent with changes in coil dimension. The radius of gyration for the polyions increases with a decrease in the ionic strength. For example the polyion radii of gyration are found to be expanded in salt-free solutions by a factor of around 2.5-3 compared to their unperturbed state. The results are also shown graphically in representative Figs. 5 and 6. One common feature observed from these plots is that the polymer coils are expanded at low ionic strength and collapse drastically with increasing ionic strength. The onset of significant collapse of the coil is found to be around a salt concentration of 0.001 mol.L^{-1} for the three polyelectrolyte samples in aqueous and in the three methanol-water mixtures investigated.

Conclusions

The present chapter reported precise measurements on the viscosities of solutions of three sodium carboxymethylcellulose samples with molecular weights of 90,000 (*DS* = 0.7), 250,000 (*DS* = 0.9), and 700,000 (*DS* = 0.9) in water and methanol-water mixtures in the absence as well as in the presence of varying concentrations of NaCl (c_s) at 35 ^{0}C. Analyses of the results on the basis of the phenomenological approach for the viscosity of polymers solutions put forward by Wolf[14] help determine the intrinsic viscosities of the investigated polyelectrolyte samples. This contribution proposed a new method for the determination of the unperturbed and the perturbed root-mean-square radii of gyration of the polyion chains from the intrinsic viscosity values obtained in solutions with varying ionic strengths in a very convenient manner. This newly proposed method has been applied to the intrinsic viscosity vs. added-salt concentration data from the system under investigation. One common feature observed from the $\langle S^2 \rangle^{1/2} = f(c_s^{-1/2})$ profiles is that the polymer coils are expanded at low ionic strength and collapse drastically with increasing ionic strength. The onset of significant collapse of the coil is found to be around a salt concentration of 0.001 mol.L^{-1} for the three polyelectrolyte samples in aqueous and in the three methanol-water mixtures investigated. The polyion radii of gyration are found to be expanded in salt-free solutions by a factor of 2.5-3 compared to their respective unperturbed states for the polyelectrolytes investigated. Thus, the method proposed here in this article for the determination of the unperturbed and perturbed root-mean-square radii of gyration of polyions simply from viscosity measurements and the information obtained for some selected carbohydrate polymers might be useful in various branches of nanoscience.

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Table 1. Parameters of Eq. (2) Describing the Composition Dependence of Viscosity of Solutions of Sodium Carboxymethylcellulose in Water and Methanol-Water Mixtures at 308.15 K in the Absence and in Presence of a Salt (NaCl)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
	Sodium Carboxymethylcellulose (M = 90,000; DS= 0.7)		
	Water		
0	1615	165.99	1.67
0.0001	1492	139.07	1.47
0.001	652	61.33	0.74
0.01	306	41.34	0.31
0.1	179	39.12	0.11
	10 vol. % methanol		
0	1478	159.19	1.68
0.0001	1370	135.91	1.53
0.001	602	56.82	0.74
0.01	271	39.72	0.32
0.1	148	37.09	0.13
	20 vol. % methanol		
0	1416	158.02	1.72
0.0001	1225	130.79	1.58
0.001	574	53.704	0.75
0.01	248	36.38	0.32
0.1	123	35.96	0.16
	30 vol. % methanol		
0	1335	130.75	1.74
0.0001	1107	126.35	1.67
0.001	546	51.07	0.77
0.01	217	36.10	0.34
0.1	112	35.55	0.16

Table 1. (contd..)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
Sodium Carboxymethylcellulose (M = 250,000; DS = 0.9)			
Water			
0	8324	355.75	0.43
0.0001	7362	327.75	0.41
0.001	3851	267.33	0.34
0.01	1486	208.77	0.23
0.1	812	193.42	0.12
10 vol. % methanol			
0	8104	348.57	0.43
0.0001	7209	324.03	0.41
0.001	3678	261.76	0.35
0.01	1409	202.74	0.23
0.1	778	189.66	0.12
20 vol.% methanol			
0	7901	340.55	0.44
0.0001	7102	323.79	0.42
0.001	3492	254.29	0.35
0.01	1350	186.10	0.22
0.1	735	170.43	0.12
30 vol.% methanol			
0	7532	325.41	0.42
0.0001	7027	317.80	0.42
0.001	3304	248.09	0.36
0.01	1294	165.78	0.20
0.1	702	153.13	0.12

Table 1. (contd..)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
Sodium Carboxymethylcellulose (M = 700,000; DS = 0.9)			
Water			
0	12700	619.72	0.28
0.0001	11400	497.81	0.26
0.001	6400	339.40	0.21
0.01	2950	260.11	0.19
0.1	1818	234.23	0.16
10 vol.% methanol			
0	12400	593.12	0.28
0.0001	10800	487.72	0.26
0.001	6250	314.33	0.21
0.01	2812	256.17	0.19
0.1	1726	224.90	0.15
20 vol.% methanol			
0	12100	553.44	0.28
0.0001	9980	476.37	0.26
0.001	5996	308.25	0.21
0.01	2680	243.19	0.19
0.1	1636	216.06	0.13
30 vol.% methanol			
0	11900	499.85	0.28
0.0001	9832	463.60	0.27
0.001	5650	303.39	0.21
0.01	2517	234.47	0.20
0.1	1519	208.47	0.12

Table 2. Unperturbed Root-mean-square Radii of Gyration, $\langle S^2 \rangle_\theta^{1/2}$, of Sodium Carboxymethylcellulose in Water and Methanol-Water Mixtures at 308.15 K

M	*DS*	$\langle S^2 \rangle_\theta^{1/2}$ (nm)			
		water	10 vol.% methanol	20 vol.% Methanol	30 vol.% methanol
90,000	0.7	14.16	13.09	12.01	11.10
250,000	0.9	29.72	29.26	28.85	28.63
700,000	0.9	60.36	58.77	57.57	56.08

Table 3. Root-mean-square Radii of Gyration, $\langle S^2 \rangle^{1/2}$ of Sodium Carboxymethylcellulose in Water and Methanol-water Mixtures in Salt-free and Salt Solutions at 308.15 K

c_s (mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)	c_s (mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)
Sodium Carboxymethylcellulose (*M* = 90,000; *DS* = 0.7)			
Water		10 vol.% methanol	
0	39.68	0	38.90
0.0001	38.40	0.0001	37.73
0.001	27.32	0.001	26.86
0.01	20.01	0.01	19.39
0.1	16.05	0.1	15.07
20 vol.% methanol		30 vol.% methanol	
0	38.88	0	38.72
0.0001	36.66	0.0001	35.85
0.001	26.84	0.001	26.80
0.01	18.96	0.01	18.33
0.1	14.16	0.1	13.97
Sodium Carboxymethylcellulose (*M* = 250,000; *DS* = 0.9)			
water		10 vol.% methanol	
0	99.2	0	98.74
0.0001	94.4	0.0001	94.12
0.001	72.5	0.001	71.35
0.01	48.7	0.01	48.08
0.1	38.11	0.1	37.65
20 vol.% methanol		30 vol.% methanol	
0	97.80	0	96.12
0.0001	93.60	0.0001	93.41
0.001	69.89	0.001	68.47
0.01	47.27	0.01	46.62

Table 3. (contd..)

c_s (mol.L^{-1})	$\langle S^2\rangle^{1/2}$ (nm)	c_s (mol.L^{-1})	$\langle S^2\rangle^{1/2}$ (nm)
Sodium Carboxymethylcellulose (M = 250,000; DS = 0.9)			
20 vol.% methanol		30 vol.% methanol	
0.1	36.81	0.1	36.20
Sodium Carboxymethylcellulose (M = 700,000; DS = 0.9)			
water		10 vol.% methanol	
0	153.10	0	152.53
0.0001	146.45	0.0001	144.11
0.001	115.36	0.001	115.06
0.01	83.96	0.01	82.91
0.1	68.80	0.1	67.62
20 vol.% methanol		30 vol.% methanol	
0	151.72	0	151.58
0.0001	140.15	0.0001	140.13
0.001	113.64	0.001	111.57
0.01	81.59	0.01	79.99
0.1	66.59	0.1	64.98

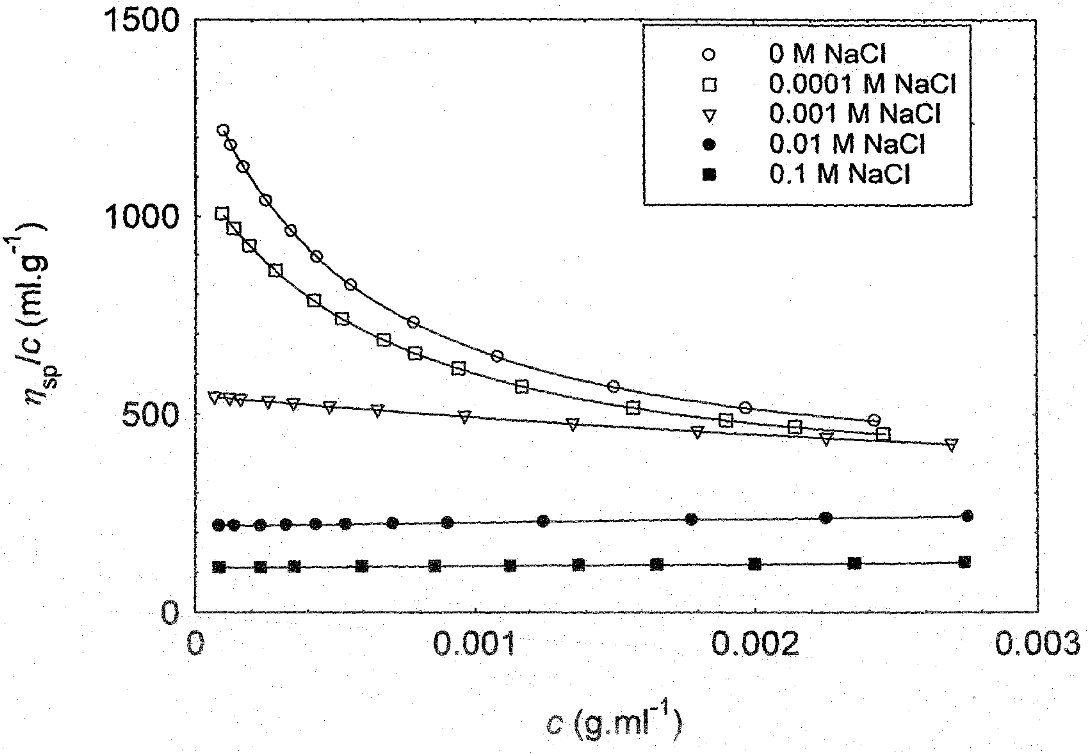

Fig. 1a. Huggins plot for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

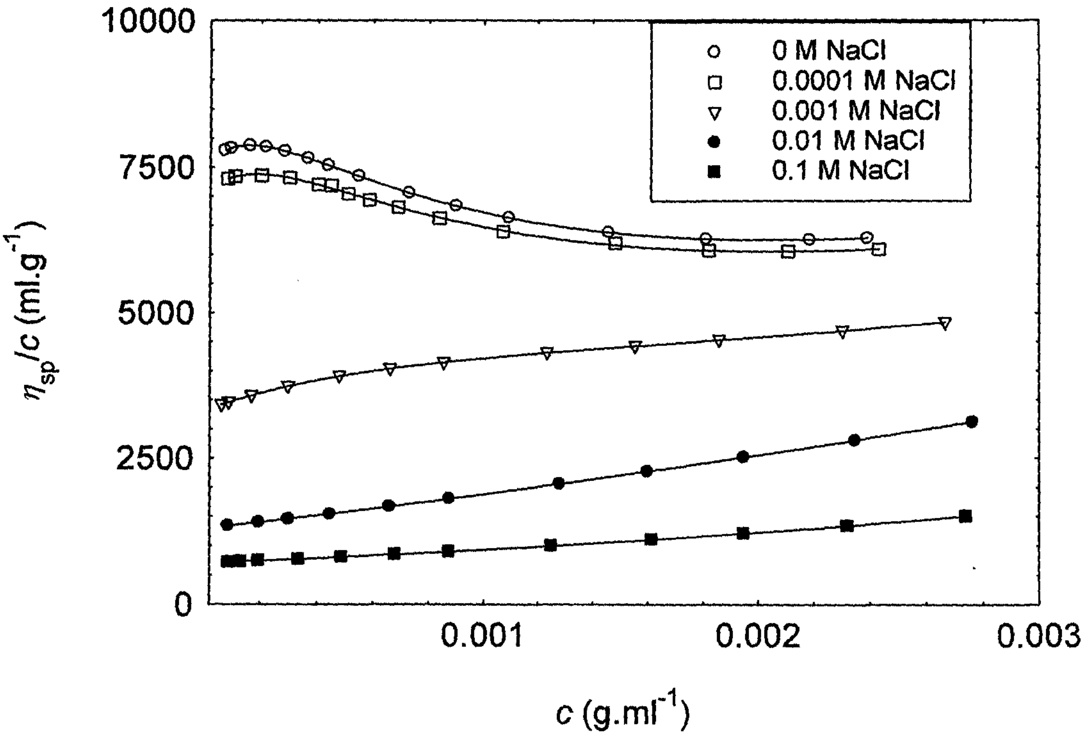

Fig. 1b. Huggins plot for solutions of sodium carboxymethylcellulose (*M* = 250,000 and *DS* = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

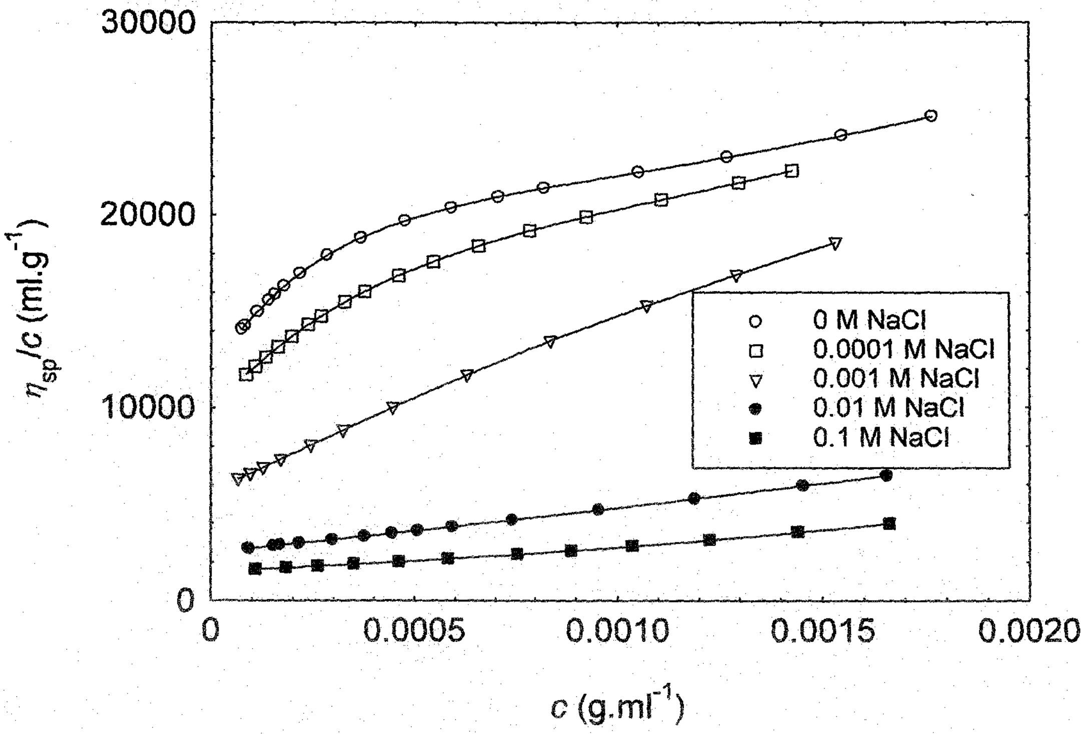

Fig. 1c. Huggins plot for solutions of sodium carboxymethylcellulose (*M* = 700,000 and *DS* = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

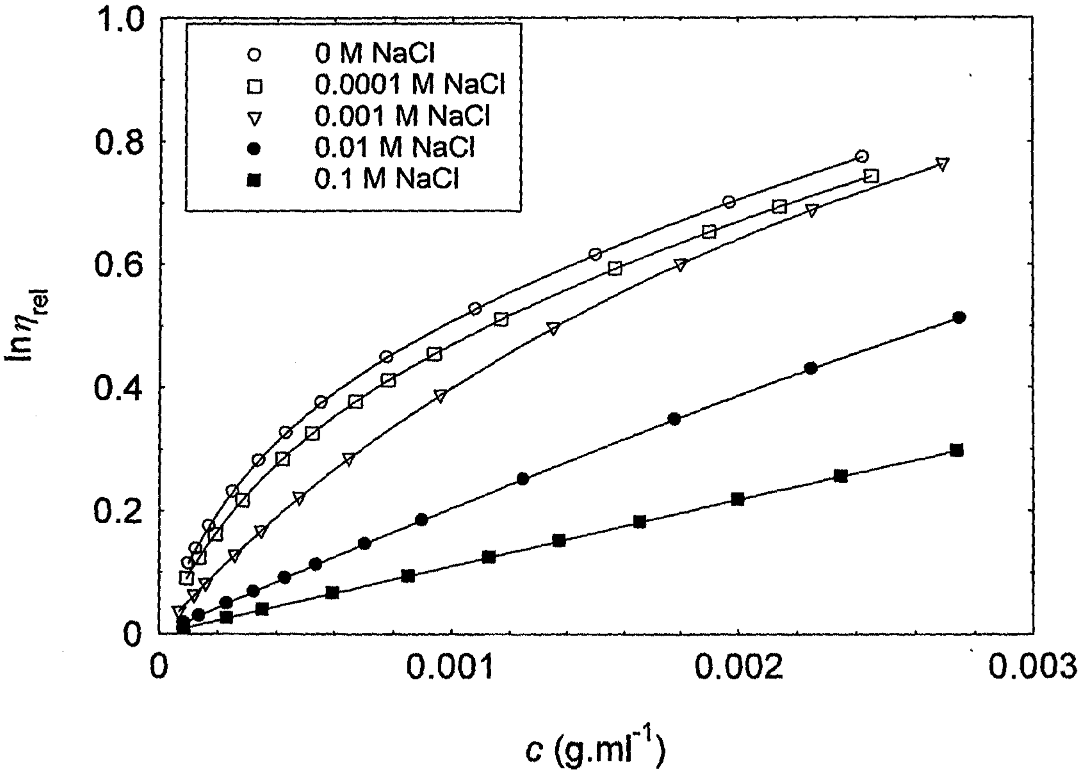

Fig. 2a. Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

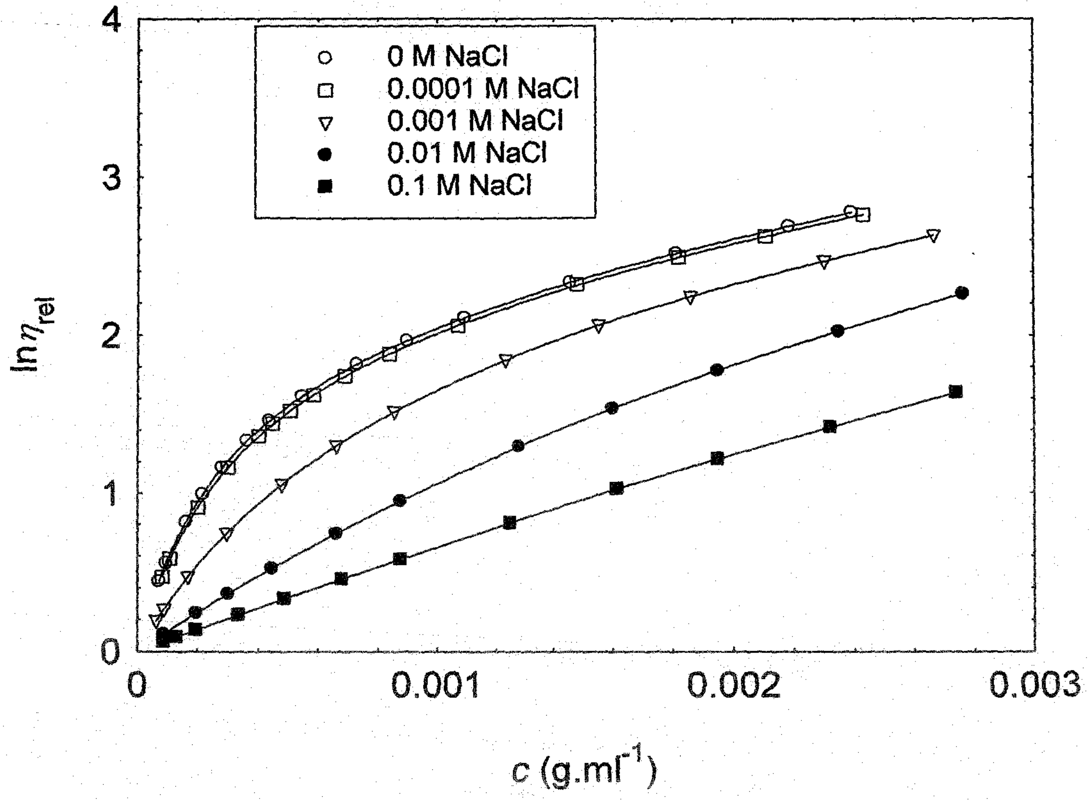

Fig. 2b. Relative viscosities of the solutions of sodium carboxymethylcellulose ($M = 250{,}000$ and $DS = 0.9$) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

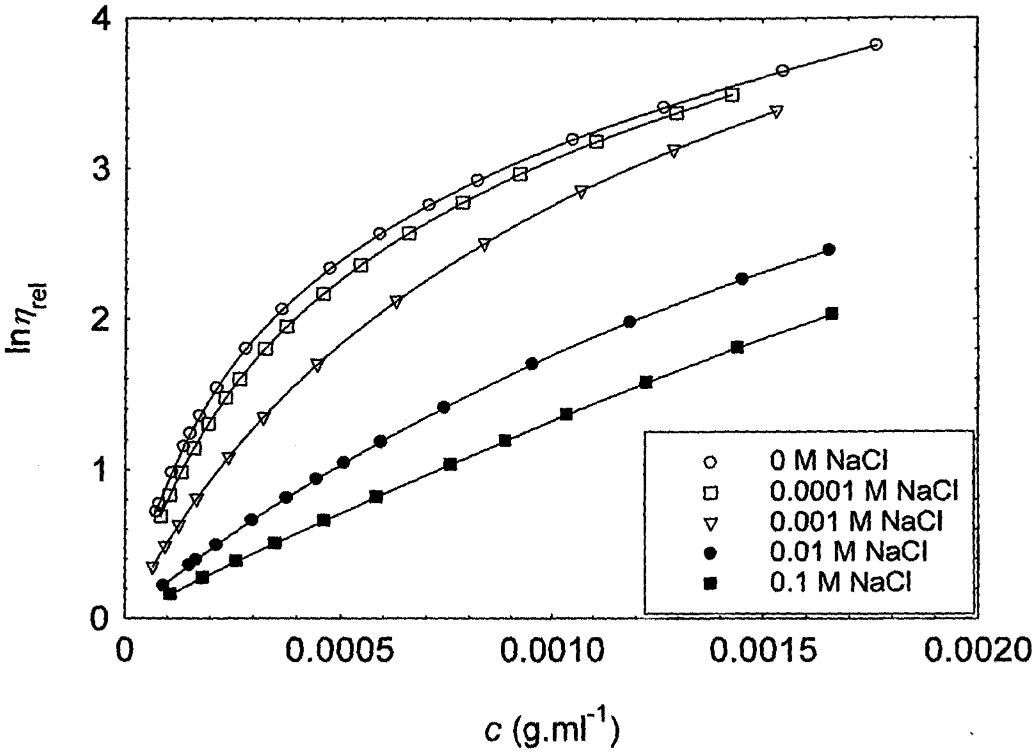

Fig. 2c. Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

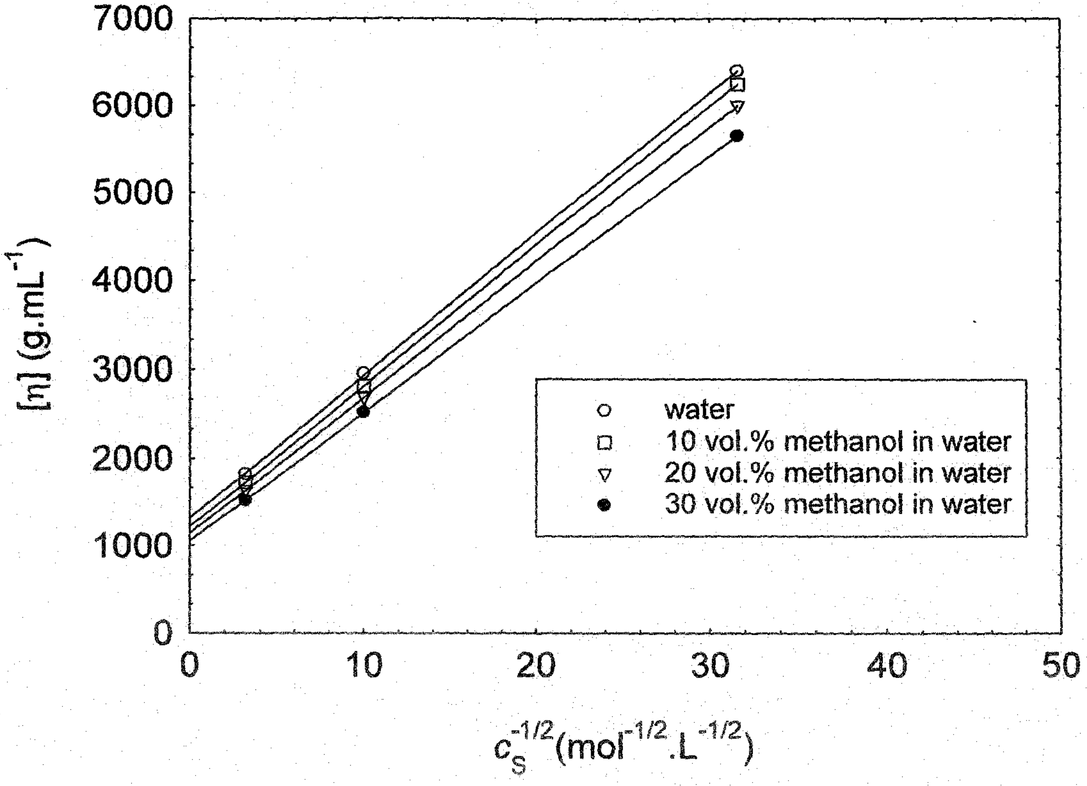

Fig. 3. Dependence of the intrinsic viscosity $[\eta]$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (*M* = 700,000 and *DS* = 0.9) in different solvent media at 308.15 K.

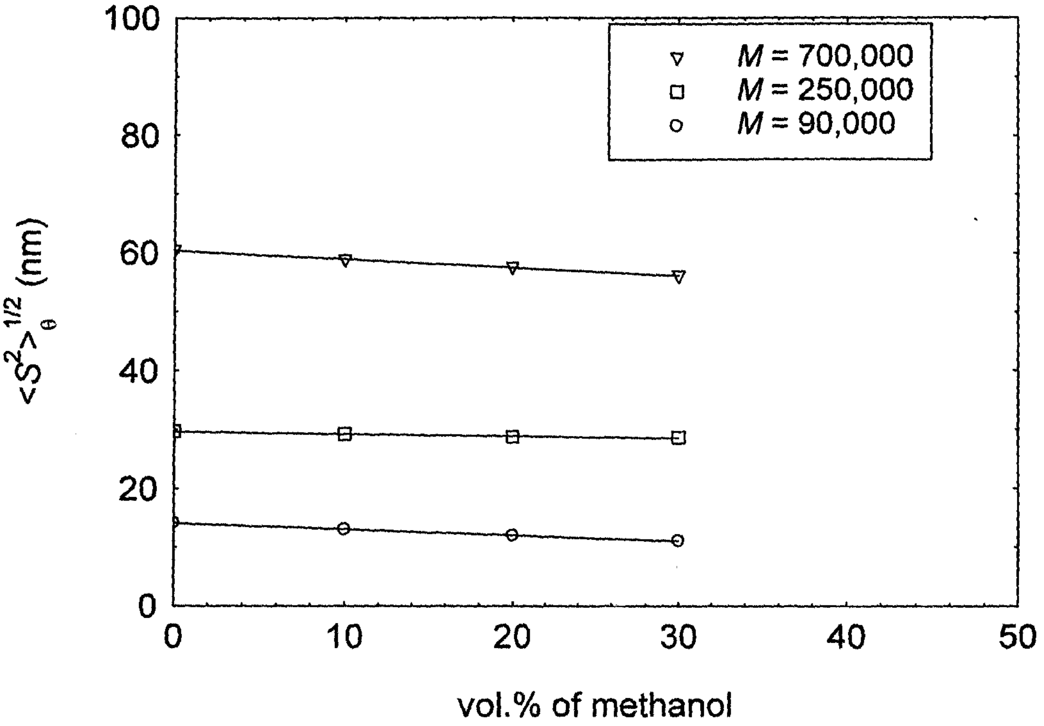

Fig. 4. Variation of the unperturbed radius of gyration for solutions of sodium carboxymethylcellulose with the solvent composition at 308.15 K.

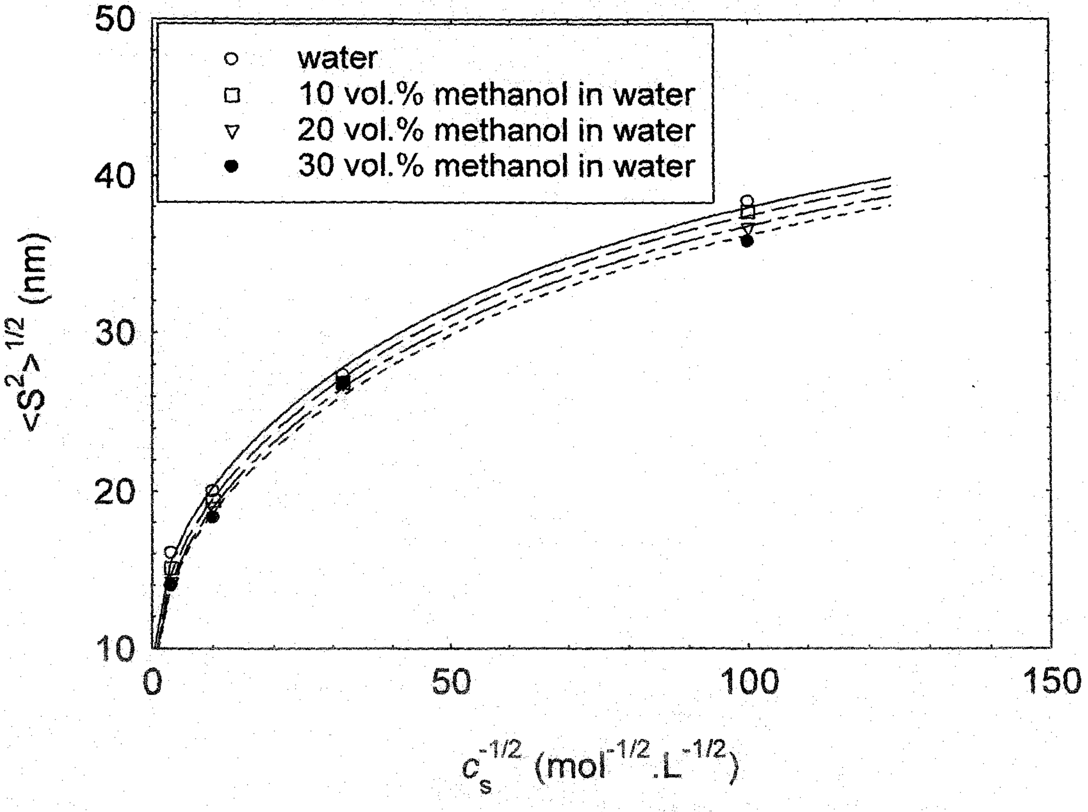

Fig. 5. Dependence of the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in different solvent media at 308.15 K.

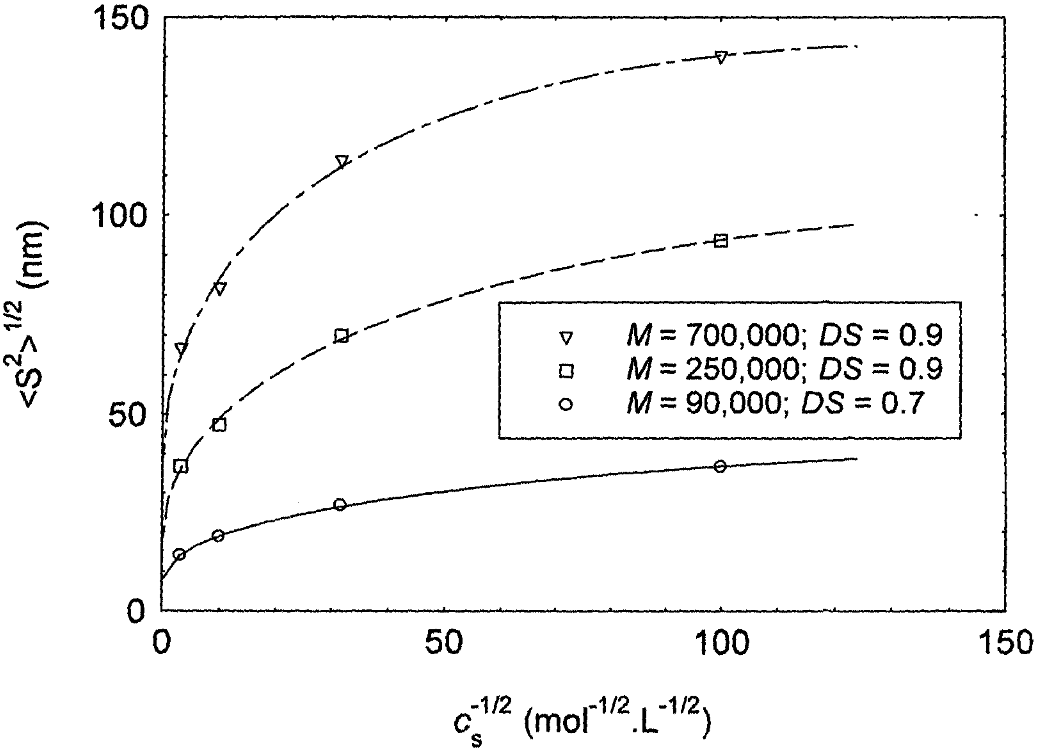

Fig. 6. Effect of the molecular weight on the dependence of the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose in methanol-water mixture containing 20 vol. % of methanol at 308.15 K.

Chapter 8

Apparent Molar Volumes of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media

Introduction

The principal factors that govern the dissolved state of polyelectrolytes in solutions are (i) the electrostatic repulsions between the ionic sites in the polyion chain and (ii) the interactions between the polyions and neighbouring counterions. The first factor is related to expansibility of the polyion chains, whereas the second is not only manifested in counterion condensation but also in the degree of solvation and the structure of the solvent in the vicinity of polyelectrolytes. Both of these factors are influenced by the relative permittivity of the solvent media. Use of a series of mixed solvents allows a systematic variation in the relative permittivity of the media, and hence enables investigation on these interactions operative in polyelectrolyte solutions. We have already investigated the influence of intramacromolecular electrostatic repulsions and the resulting coiling/expansion of the polyion chains from viscosity measurements on sodium carboxymethylcellulose in methanol-water mixtures. In this chapter, we report the apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixtures with a view to investigate the polyion-counterion interactions as well as the solvation behaviour of the counterions.

Experimental

Methanol (Acros Organics, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.77728 g.cm^{-3} and a co-efficient of viscosity of 0.4747 mPa.s at 308.15 K; these values are in good agreement with the literature values.[1] Triply distilled water with a specific conductance of less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents.

Sodium carboxymethylcellulose was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 90,000 with a degree of substitution (DS) of 0.70, and these values agree well with those obtained from physiochemical characterization in the present study.

Density measurements were carried out on an Anton Paar DMA-4500M digital precision densimeter. The precision of the density measurements was $3\cdot10^{-5}$ g.cm^{-3} Calibration of the densimeter was done at each temperature using dry air under ambient pressure, and deionized triply distilled water. Densities of methanol-water mixtures at 298.15, 303.15, 308.15 and 313.15 K are given in Table 1.

Results and Discussion

Apparent Molar Volumes

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

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

where c_p is the polyelectrolyte concentration (in monomolarity), M the molecular mass of the repeating unit of sodium carboxymethylcellulose with a degree of substitution (*DS*) of 0.7, ρ the density of the solution and ρ_0 the density of the solvent.

Variations of Apparent Molar Volumes with Polyelectrolyte Concentration

Figs. 1 – 3 show the variations of apparent molar volumes as a function of the square root of the monomolar concentration of sodium carboxymethylcellulose in methanol-water mixtures containing 10, 20 and 30 volume percent of methanol at 298.15, 303.15, 308.15, and 313.15 K. Within the concentration ranges investigated here, the ϕ_v *vs.* $\sqrt{c}$ plots are found to be linear and, moreover, as $\sqrt{c}$ is increased, ϕ_v increased marginally. Similar linear increases for ϕ_v with concentration have been previously reported by Conway and Desnoyers,[2] Lawrence and Conway,[3] Ise and Okubo[4] and Tondre and Zana[5] for various polyelectrolytes in aqueous solutions although the insensitivity of ϕ_v toward concentration was also reported[4] for salts of polystyrenesulfonic 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 methanol-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. $\sqrt{c}$ plots.

The Limiting Partial Molar Volumes

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

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \tag{2}$$

where S_v is the experimental slope. The values of ϕ_v^0 (= $\bar{V}_2^0$) and S_v are given Table 2. The correlation coefficients (r) of the regression analyses were always found to be greater than or equal to 0.9723.

The limiting partial molar volumes are found to decrease as the medium becomes richer in methanol at a given temperature, whereas in a given mixed solvent medium, $\bar{V}_2^0$ values are found to increase with increasing temperature.

Effect of Medium and Temperature on the Limiting Partial Molar Volumes

The limiting partial molar volume of sodium carboxymethylcellulose decreases with increasing amount of methanol in the methanol-water mixtures at any given temperature (Table 2), and this might be due to more efficient polyion-coiling driven by greater counterion condensation as the medium becomes richer in methanol. An increase in the temperature, on the other hand, increases the limiting partial molar volume of sodium carboxymethylcellulose in a given mixed solvent medium as can be seen from Table 2. This might be ascribed to the growing importance of the contribution to the partial molar volume due to a temperature-induced desolvation of the counterions leading to more counterion binding at higher temperatures as observed earlier from conductivity measurements (Chapter 4).

Conclusions

The present investigation indicates that in methanol-water mixed solvent media counterion binding would become quite appreciable as the concentration of the polyelectrolyte is increased, thereby weakening the ion-solvent interactions. Influences of the medium and the temperature on the limiting partial molar volumes have also been discussed.

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Table 1. Densities (ρ) of Methanol-Water Mixed Solved Media at 298.15, 303.15, 308.15, and 313.15 K

T (K)	ρ (g.cm^{-3})		
	Vol.% of Methanol		
	10	20	30
298.15	0.98297	0.96963	0.95620
303.15	0.98138	0.97688	0.95393
308.15	0.97973	0.96632	0.95160
313.15	0.97791	0.96407	0.94893

Table 2. Limiting Partial Molar Volumes ($\bar{V}_2^0$) of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solved Media at 298.15, 303.15, 308.15, and 313.15 K

T(K)	$\bar{V}_2^0$ (cm^3.mol^{-1})		
	Vol.% of Methanol		
	10	20	40
298.15	181.60	178.75	175.93
303.15	183.45	180.84	177.44
308.15	184.86	181.93	178.91
313.15	186.53	183.50	180.15

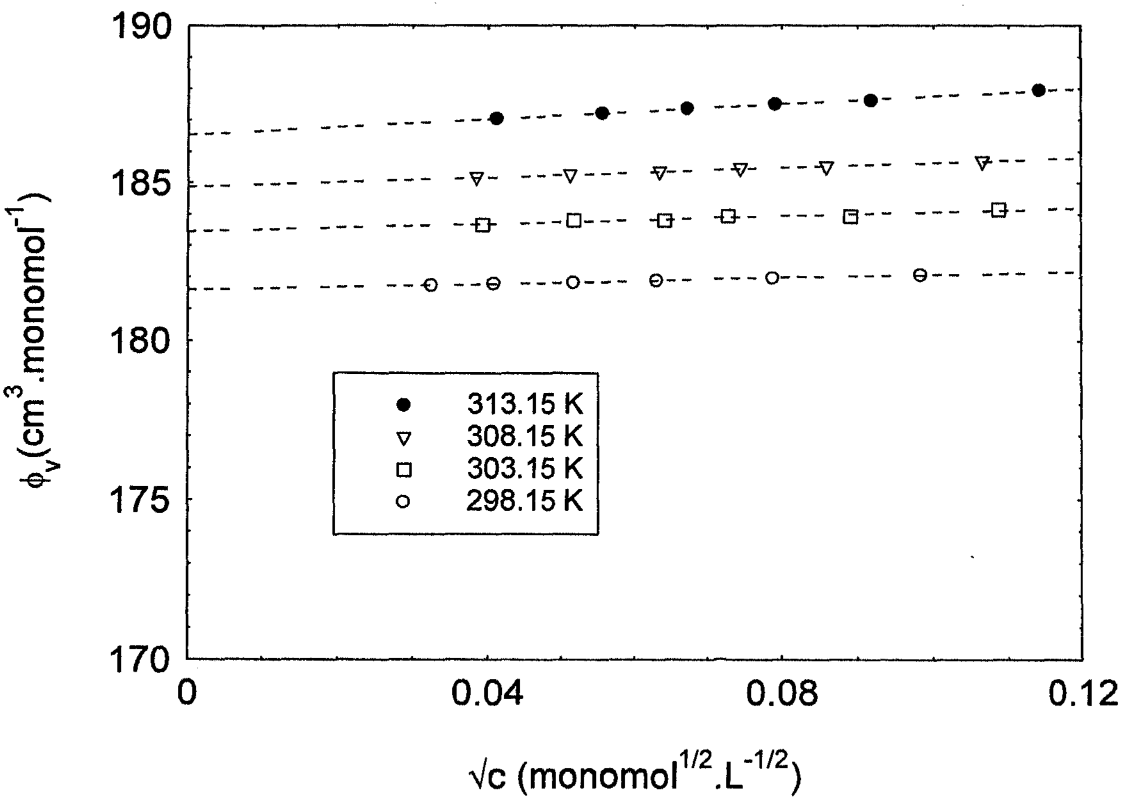

Fig. 1. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 10 vol. % of methanol at different temperatures.

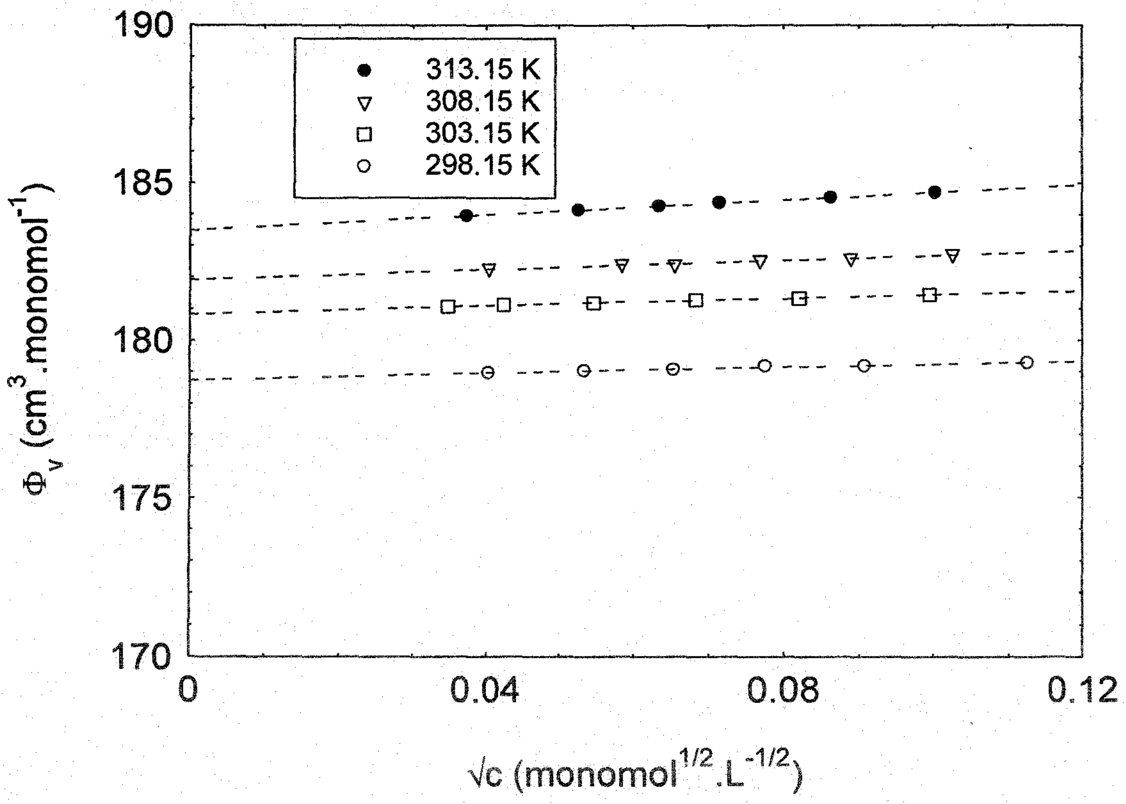

Fig. 2. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 20 vol. % of methanol at different temperatures.

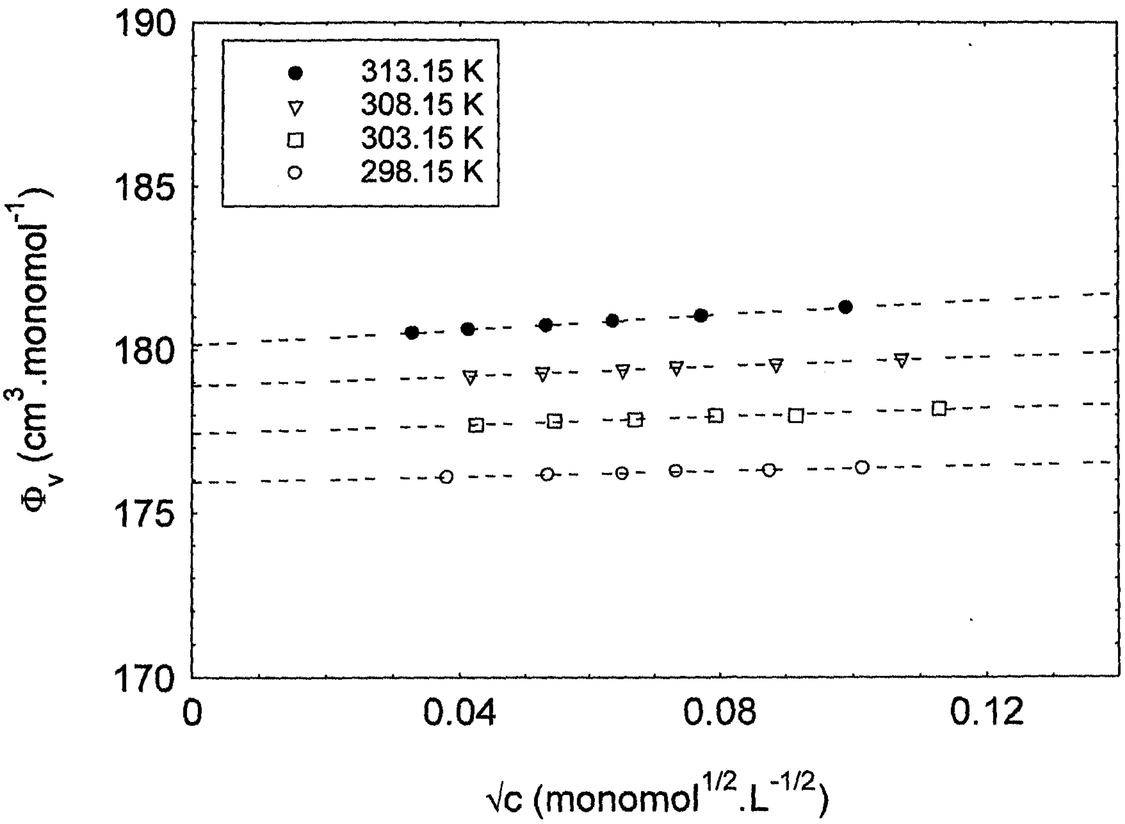

Fig. 3. Apparent molar volumes of sodium carboxymethylcellulose in methanol-water mixed solvent medium containing 30 vol. % of methanol at different temperatures.

Chapter 9

Concluding Remarks

Polyelectrolytes demonstrate numerous interesting properties that are now being widely investigated in many laboratories. Many significant 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 a selected polyelectrolyte sodium carboxymethylcellulose in methanol-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. Electrical conductivities of the polyelectrolyte in presence of salts underlined the importance of various factors namely, electrophoretic countercurrent, solvodynamic interactions, salt-induced conformational changes in the polyion structure and hence a concomitant change in the apparent charge of the polyion *etc.* in polyelectrolytes. The method of isoionic dilution has been successfully employed for determining the intrinsic viscosity and the Huggins constant of sodium carboxymethylcellulose in methanol–water mixed solvent media. Intermolecular and intramolecular contribution has also been separated from purely experimental point of view in the said mixed solvent media.

Determination of intrinsic viscosity in absence of added salt had been very problematic for a long time because of the polyelectrolyte effect. However we have successfully obtained intrinsic viscosity for three samples of the said polyelectrolyte by using Wolf approach both in absence and presence of an added electrolyte. We have proposed a new method for the determination of the unperturbed and the perturbed root-mean-square radii of gyration of the polyion chains from the intrinsic viscosity values. This new approach may be useful in various branches of nanoscience.

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 polyeletrolyte 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.

Annexure

Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Methanol-Water Mixtures at 298.15, 308.15, and 318.15 K

Introduction

In order to analyse the conductivity data of sodium carboxymethylcellulose in methanol-water mixed solvent media, the limiting ionic equivalent conductivities of sodium ion in relevant mixtures are essential. We have, therefore, performed electrical conductivity measurement on tetrabutylammonium bromide (Bu_4NBr), sodium tetraphenylborate ($NaBPh_4$) and sodium bromide (NaBr) in methanol-water mixtures at 298.15, 308.15, and 318.15 K in order to obtain precise temperature-dependent single-ion conductivities since these data are not available in the literature.

Experimental

Materials

Methanol (Acros Organics, 99.9% pure) was dried over molecular sieves and distilled fractionally. The middle fraction was collected and redistilled. The purified solvent had a density of 0.77728 g.cm^{-3} and a coefficient of viscosity of 0.4747 mPa·s at 308.15 K; these values are in good agreement with the literature values.[1,2] Triply distilled water with a specific conductance of less than 10^{-6} S·cm^{-1} at 308.15 K was used for the preparation of the mixed solvents. The physical properties of methanol-water mixed solvents used in this study at 298.15, 308.15, and 318.15 K are reported in Table 1. The relative permittivities of methanol-water mixtures at the experimental temperatures were obtained from literature.[3]

All of these salts were of Fluka purum or puriss grade. Tetrabutylammonium bromide (Bu_4NBr) was purified by recrystallization from acetone and the recrystallized salt was dried in vacuo at 333.15 K for 48 h. Sodium tetraphenylborate ($NaBPh_4$) was recrystallized three times from acetone and then dried under vacuum at 353.15 K for 72 h. Sodium bromide

(NaBr) was dried in vacuo for 72 h immediately prior to use and was used without further purification.

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 of cell constant 1.15 cm^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers[4] using aqueous potassium chloride solutions. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier[5,6] and also in Chapter II. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 cm^3 capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the salt solutions.

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

Results and Discussion

Data Analysis: Limiting Ionic Equivalent Conductances

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.[7,8] For a given set of conductivity values (c_j, Λ_j; $j = 1, \ldots, n$), three adjustable parameters - the limiting molar conductivity (Λ^0), association constant (K_A), and the association diameter (R), are derived from the following set of equations :

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

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

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{3}$$

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

$$\beta = \frac{e^2}{\varepsilon k_B T} \tag{5}$$

$$K_A = K_R(1+K_S) \tag{6}$$

where *RX* is the relaxation field effect, *EL* is the electrophoretic countercurrent, γ is the fraction of unpaired ions, and α is the fraction of contact-pairs, K_A is the overall pairing constant evaluated from the association constants of contact-pairs, K_S, of solvent-separated pairs, K_R, ε is the relative permittivity of the solvent, *e* is the protonic charge, k_B is the Boltzmann constant, k^{-1} is the radius of the ion atmosphere, *c* is the molarity of the solution, *f* is the activity coefficient, *T* is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations were performed on a computer using the program as suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation[9] of the data. Input for the program is the set (c_j, Λ_j; $j = 1, \ldots, n$), n, ε, η, T, initial value of Λ^0, and an instruction to cover a preselected range of *R* values.

In practice, calculations are made by finding the values of Λ^0 and α which minimize the standard deviation, σ,

$$o^2 = \sum[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 /(n-2) \tag{7}$$

for a sequence of *R* values and then plotting σ against *R*; the best-fit *R* corresponds to the minimum in σ vs. *R* curve. However,for salts investigated here, sice a preliminary scan using incremental *R* values from 4 to 20 produced no significant minima in the σ vs. *R* curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and *d* is given by

$$d = 1.183(M/\rho_0)^{1/3} \tag{8}$$

where M is the molecular weight of the solvent and ρ_0 is its density.The values of Λ^0, K_A, and R obtained by this procedure are reported in Table 1.

Division of Limiting Equivalent Conductances: Limiting Ionic Equivalent Conductivities

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

The limiting ionic conductivities have been evaluated from the division of the Λ^0 values of Bu_4NBPh_4 using the following relationship:

$$\lambda^0(Bu_4N^+) = 0.517\,\Lambda^0(Bu_4NPh_4B) \qquad (9)$$

as described in the literature.[10,11]

The limiting molar conductivity (Λ^0) of the "reference electrolyte" Bu_4NBPh_4 was obtained by considering the Kohlrausch rule that allows the calculation of the Λ^0 value for a given electrolyte by the appropriate combination of others. The Λ^0 values of Bu_4NBr, $NaBPh_4$ and NaBr obtained in the present solvent media have been used to obtain the Λ^0 value of Bu_4NBPh_4 through the following equation:

$$\Lambda^0(Bu_4NBPh_4) = \Lambda^0(Bu_4NBr) + \Lambda^0(NaPh_4B) - \Lambda^0(NaBr) \qquad (10)$$

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

Ion Association Behaviour

The association constants (K_A) listed in Table 1 for all these systems are practically negligible (*i.e.*, $K_A < 10$). So, the numerical values of K_A should not be taken seriously.[12] One can only conclude that all of these three electrolytes exist as free ions in both the solvent mixtures in the temperature range 298.15 to 318.15 K. This is expected because the relative parmittivities of the solvent mixtures are fairly high ($60.99 \leq \varepsilon \leq 75.09$).

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

In both the mixed solvent media, the limiting ionic equivalent conductances decreases in the order: $\lambda^0_{Br^-} > \lambda^0_{Na^+} > \lambda^0_{Bu_4N^+} > \lambda^0_{Ph_4B^-}$ at each temperature indicating that the sizes of these ions as they exist in solutions follow the order: $Br^- < Na^+ < Bu_4N^+ < Ph_4B^-$. Another interesting observation is that the limiting ionic equivalent conductances of all ions decrease in going form 10 volume percent of methanol to 30 volume percent of methanol in the mixture at all temperatures investigated.

The limiting equivalent conductances of the electrolytes as well as the single-ion conductivity values increase appreciably with temperature.The effect of temperature on $\lambda^0_{Na^+}$ and $\lambda^0_{Br^-}$ ions is more pronounced as compaired to that as $\lambda^0_{Bu_4N^+}$ and $\lambda^0_{Ph_4B^-}$ in the present mixed solvent media.

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Table 1. Derived Conductivity Parameters of Electrolytes in Methanol-Water Mixtures Containing 10, 20 and 30 Volume Percent of Methanol at 298.15, 308.15, and 318.15 K

T(K)	Λ^0 (S.cm^2.mol^{-1})	K_A /(dm^3.mol^{-1})	$R/\overset{0}{A}$	$\sigma\%^a$
10 Vol. % of Methanol				
Bu_4NBr				
298.15	81.16 ± 0.07	2.72 ± 0.06	9.99	0.10
308.15	95.30 ± 0.07	3.20 ± 0.05	10.09	0.08
318.15	114.75 ± 0.28	3.81 ± 0.18	10.18	0.27
$NaPh_4B$				
298.15	66.87 ± 0.02	4.88 ± 0.04	9.50	0.01
308.15	75.45 ± 0.02	4.83 ± 0.05	9.59	0.01
318.15	91.86 ± 0.02	5.79 ± 0.03	9.68	0.01
NaBr				
298.15	114.46 ± 0.04	1.41 ± 0.01	5.95	0.05
308.15	134.88 ± 0.05	1.50 ± 0.02	5.95	0.05
318.15	163.50 ± 0.07	1.61 ± 0.02	5.96	0.05
20 Vol. % of Methanol				
Bu_4NBr				
298.15	65.56 ± 0.05	2.74 ± 0.05	10.09	0.08
308.15	79.87 ± 0.06	2.34 ± 0.05	10.09	0.09
318.15	100.19 ± 0.09	2.40 ± 0.06	10.10	0.10
$NaPh_4B$				
298.15	53.14 ± 0.02	4.87 ± 0.06	9.59	0.01
308.15	67.33 ± 0.19	4.16 ± 0.06	9.59	0.07
318.15	85.18 ± 0.02	5.30 ± 0.03	9.68	0.01
NaBr				
298.15	93.85 ± 0.04	1.41 ± 0.02	6.04	0.05
308.15	118.20 ± 0.08	1.82 ± 0.03	6.04	0.08
318.15	153.22 ± 0.12	3.38 ± 0.04	6.05	0.08
30 Vol. % of Methanol				
Bu_4NBr				
298.15	59.94 ± 0.04	8.05 ± 0.06	10.18	0.05
308.15	71.05 ± 0.04	8.95 ± 0.05	10.18	0.04
318.15	93.08 ± 0.04	9.41 ± 0.04	10.19	0.03

Table 1. (contd..)

T(K)	Λ^0(S.cm^2.mol^{-1})	K_A/(dm^3.mol^{-1})	$R/\overset{0}{A}$	$\sigma\%^a$
		30 Vol. % of Methanol		
		NaPh$_4$B		
298.15	44.46 ± 0.02	6.25 ± 0.09	9.68	0.01
308.15	63.08 ± 0.05	6.44 ± 0.13	9.68	0.01
318.15	78.17 ± 0.03	6.28 ± 0.06	9.69	0.01
		NaBr		
298.15	83.67 ± 0.05	1.22 ± 0.03	6.13	0.07
308.15	106.55 ± 0.08	1.55 ± 0.04	6.13	0.08
318.15	142.04 ± 0.10	4.60 ± 0.04	6.14	0.07

[a] $\sigma\% = 100\sigma / \Lambda^0$

Table 2. Limiting Ionic Conductances in Methanol-Water Mixtures Containing 10, 20 and 30 Vol. % of Methanol at 298.15, 308.15 and 318.15 K

$T(K)$	$\lambda_{\pm}^{0}$ (S.cm^2.mol^{-1})			
	Na^+	Bu_4N^+	Br^-	Ph_4B^-
		10 Vol. % of Methanol		
298.15	50.66	17.36	63.80	16.21
308.15	58.12	18.54	76.76	17.33
318.15	71.04	22.29	92.46	20.82
		20 Vol. % of Methanol		
298.15	41.14	12.85	52.71	12.00
308.15	53.32	14.99	64.88	14.01
318.15	69.65	16.62	83.57	15.53
		30 Vol. % of Methanol		
298.15	34.45	10.72	49.22	10.01
308.15	49.76	14.26	56.79	13.32
318.15	64.06	15.10	77.98	14.11

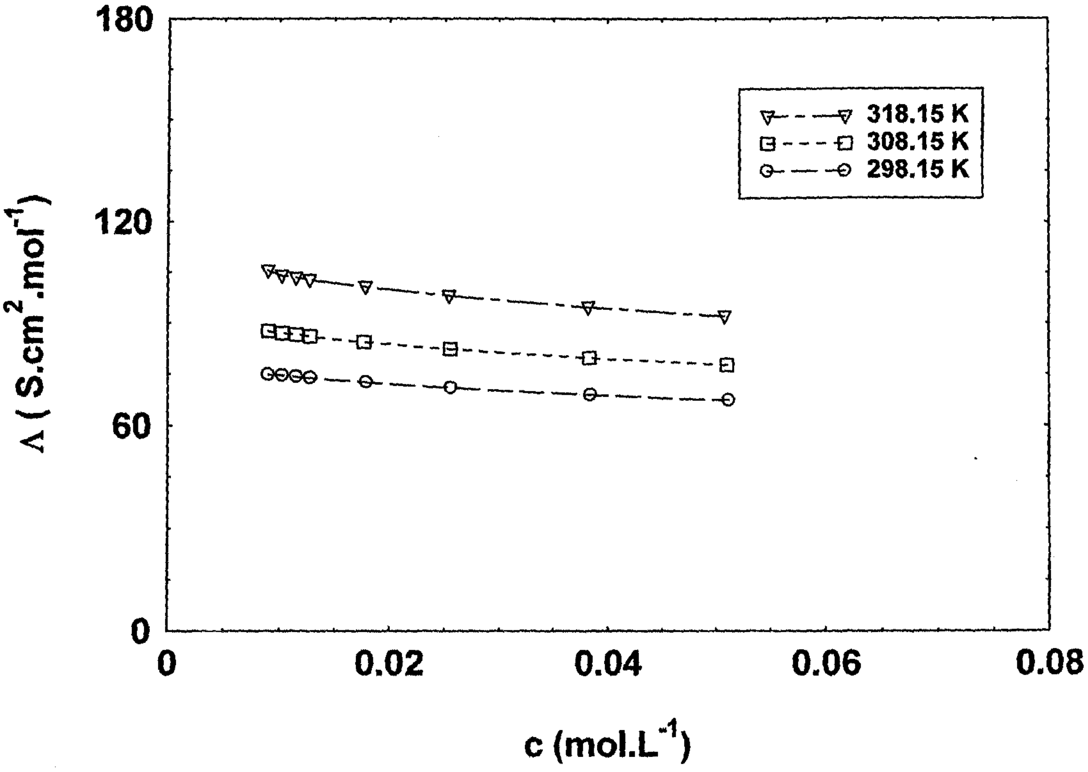

Fig. 1. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

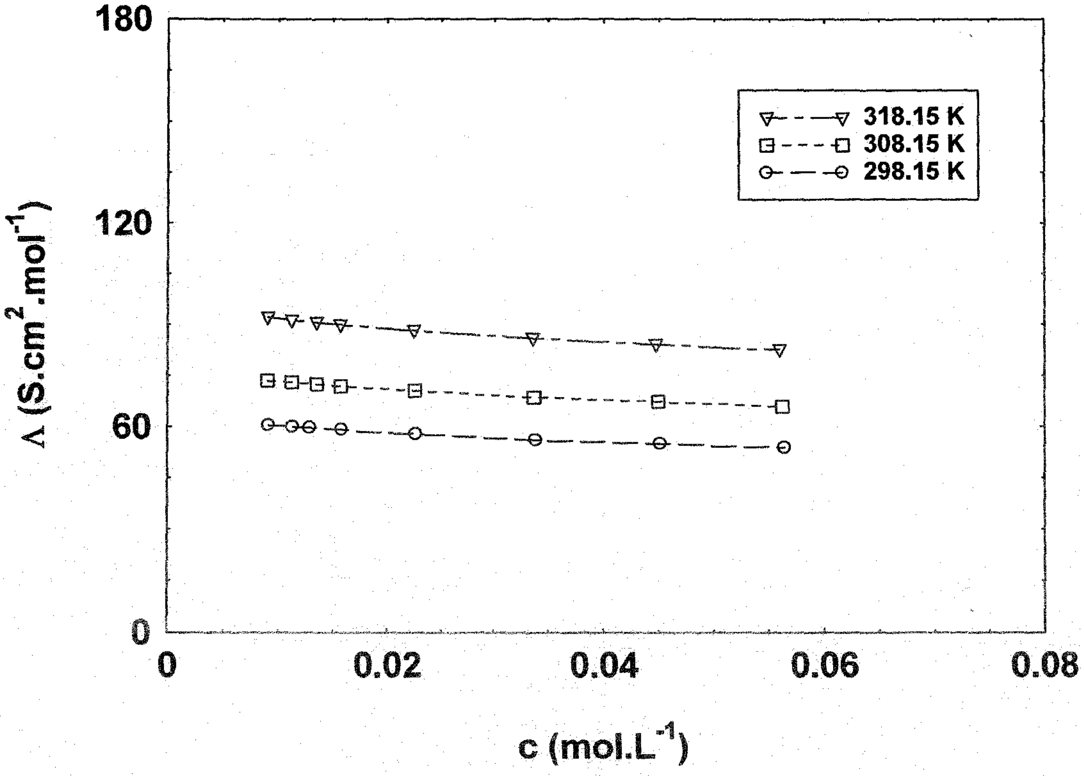

Fig. 2. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 20 vol. % methanol at different temperatures.

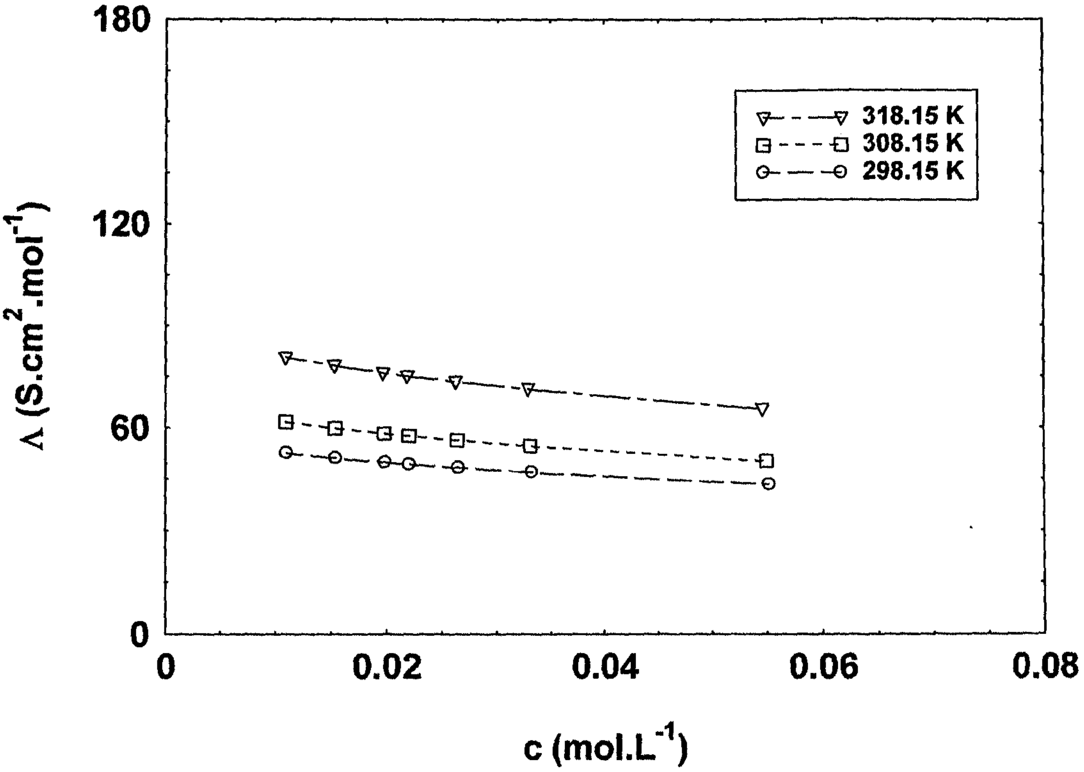

Fig. 3. Concentration dependence of the equivalent conductance of tetrabutylammonium bromide (Bu_4NBr) in methanol-water mixture containing 30 vol. % methanol at different temperatures.

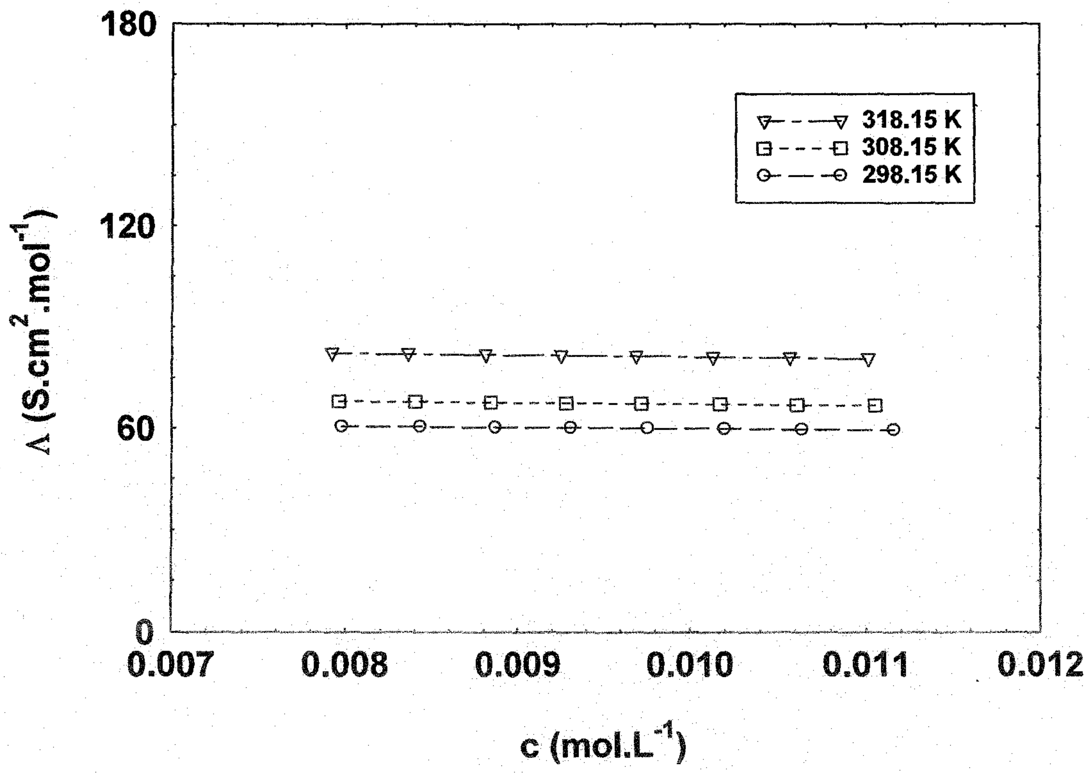

Fig. 4. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

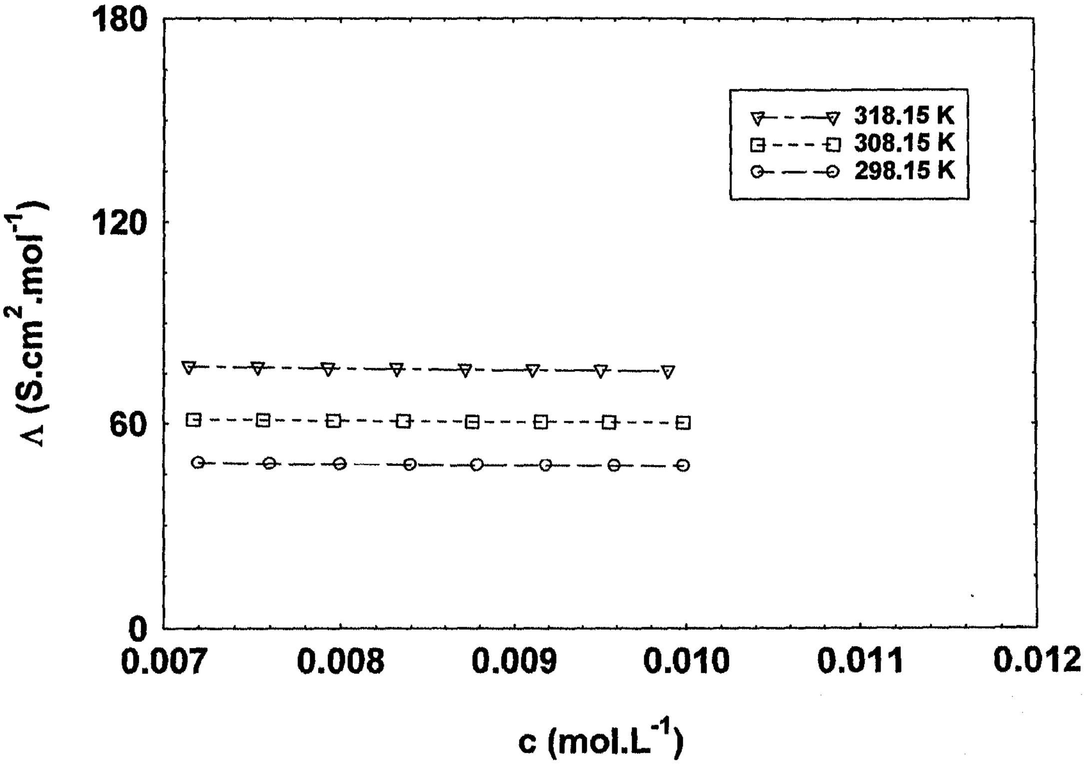

Fig. 5. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 20 vol. % methanolat different temperatures.

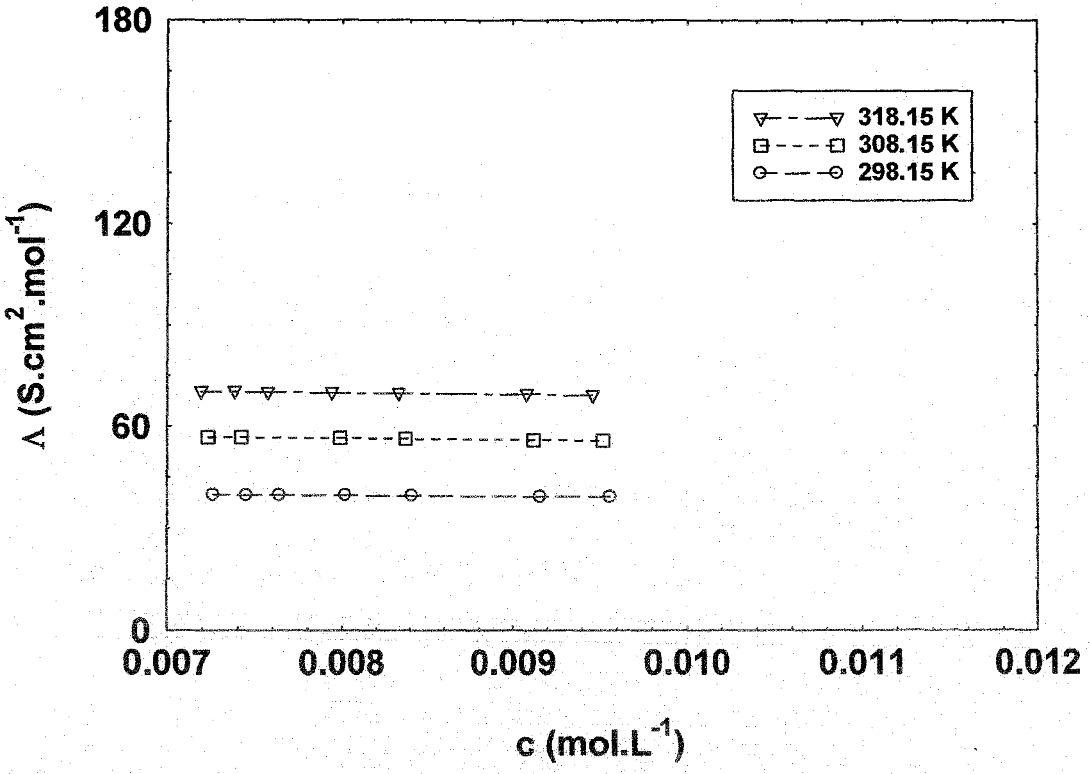

Fig. 6. Concentration dependence of the equivalent conductance of sodium tetraphenylborate ($NaPh_4B$) in methanol-water mixture containing 30 vol. % methanol at different temperatures.

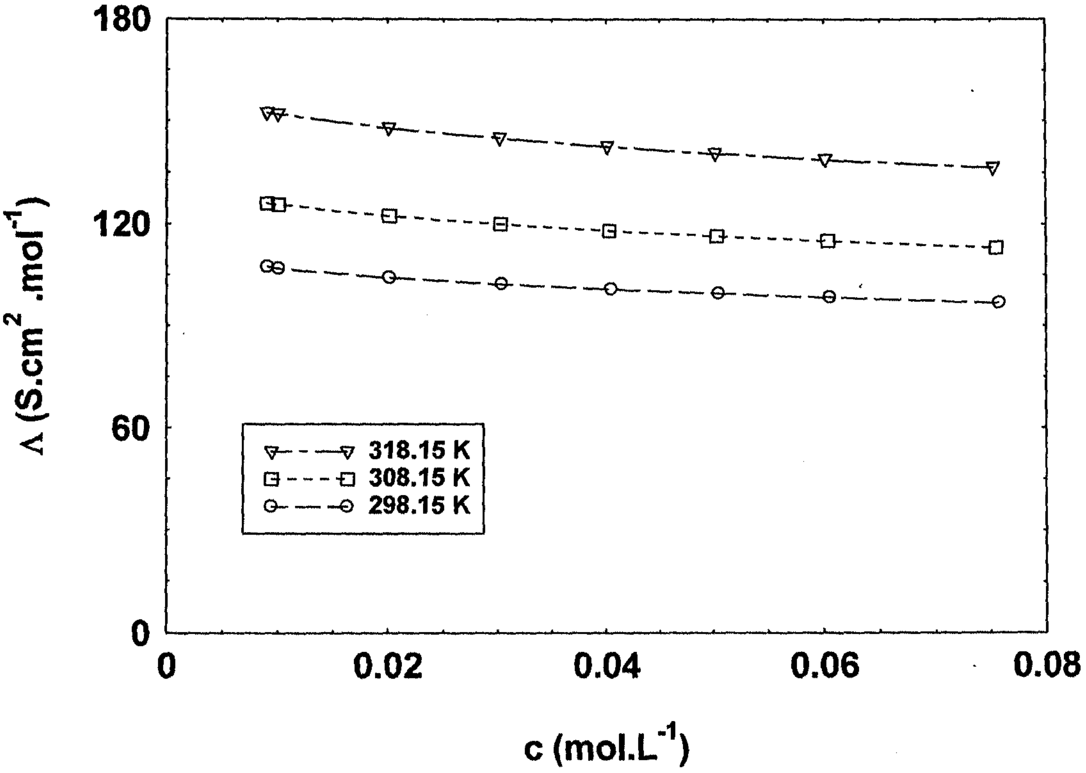

Fig. 7. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 10 vol. % methanol at different temperatures.

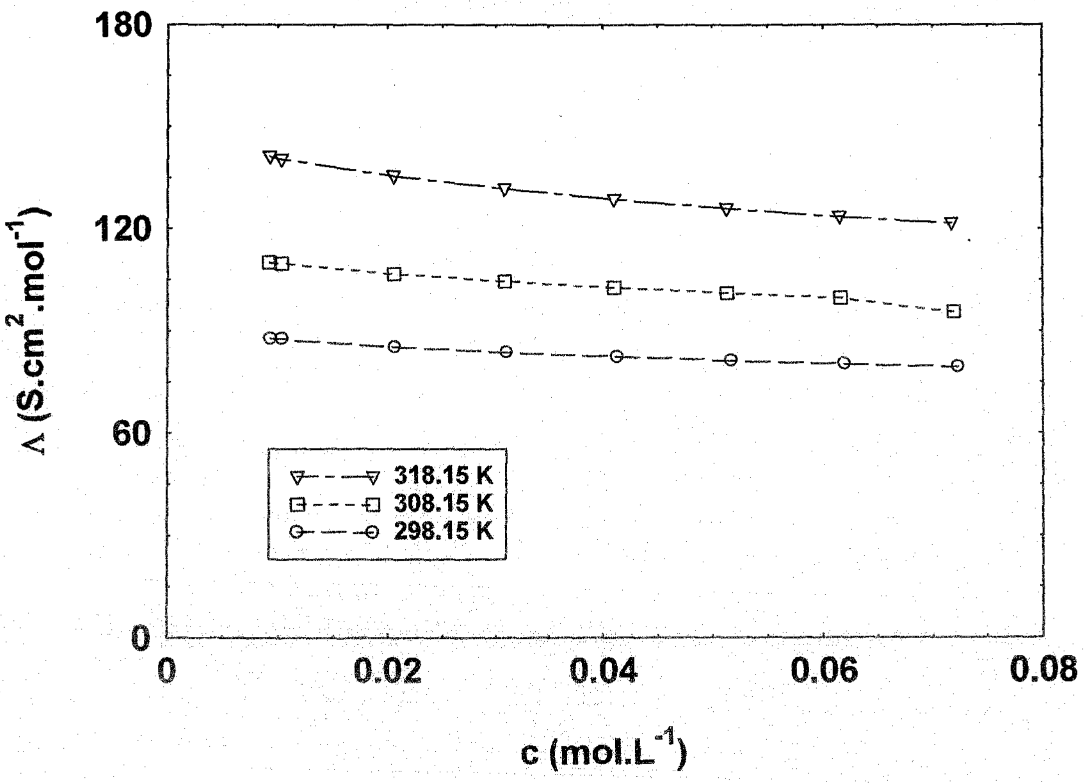

Fig. 8. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 20 vol. % methanol at different temperatures.

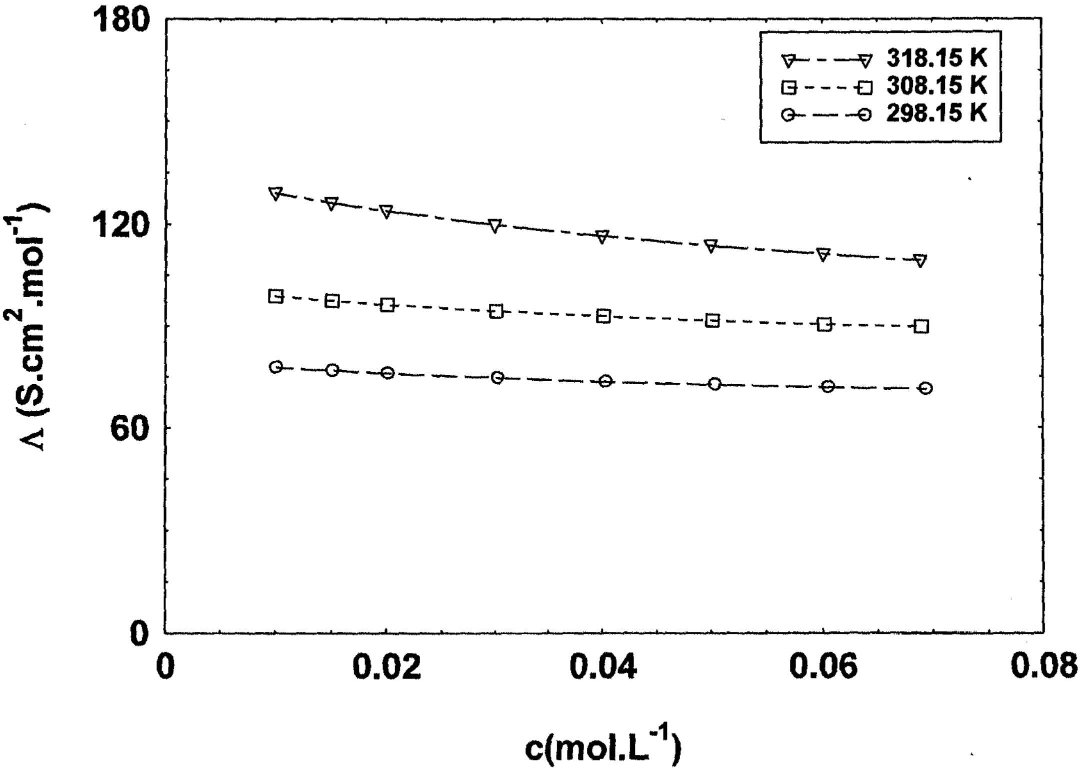

Fig. 9. Concentration dependence of the equivalent conductance of sodium bromide (NaBr) in methanol-water mixture containing 30 vol. % at different temperatures.

Publications

List of Papers Published

1. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Methanol (1) + Water (2) Mixtures at (298.15, 308.15, and 318.15) K, A. Chatterjee and B. Das, *J. Chem. Eng. Data.*, **51**, 1352 (2006).

2. Electrical Conductances of Tetrabutylammonium Bromide, Sodium Tetraphenylborate, and Sodium Bromide in Ethylylene Glycol (1) + Water (2) Mixtures at (298.15, 303.15, 308.15, and 318.15) K, R. Sharma, C. Das, A. Chatterjee and B. Das, *J. Chem. Eng. Data.*, **54**, 1899 (2009).

3. Polyion–counterion interaction behavior for Sodium Carboxymethylcellulose in methanol–water mixed solvent media, A. Chatterjee, B. Das and C. Das, *Carbohydrate Polym.*, **87**, 1144 (2012).

4. Electrical Conductances of Ionic Liquids 1-Butyl-3-propyl imidazolium Bromide ([BPim][Br]) and 1-Butyl-3-propyl benzimidazolium Bromide ([BPbim][Br]) in Water, Methanol, and Acetonitrile at 308.15, 313.15, and 318.15 K S. Gupta, A. Chattejee, B. Das, S. Das and B. Basu, *J. Chem. Eng. Data.*, communicated.

5. Intrinsic Viscosity and Radius of Gyration of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media, A. Chatterjee and B. Das, *Carbohydrate Polym.*, communicated.