



Polyion–counterion interaction behavior for sodium carboxymethylcellulose in methanol–water mixed solvent media

Amritendu Chatterjee^a, Bijan Das^{a,*}, Chanchal Das^b

^a Department of Chemistry, North Bengal University, Darjeeling 734 013, India

^b Department of Chemistry, Sikkim Government College, Tadong, Gangtok, 737 102, India

ARTICLE INFO

Article history:

Received 22 June 2011

Received in revised form 25 August 2011

Accepted 27 August 2011

Available online 3 September 2011

Keywords:

Electrical conductivity

Sodium carboxymethylcellulose

Methanol–water mixed solvent media

Counterion condensation

Scaling theory approach

ABSTRACT

Precise measurements on the electrical conductivities have been reported for solutions of sodium carboxymethylcellulose in methanol–water mixed solvent media. The conductivity vs. concentration data have been analyzed on the basis of the scaling theory approach for semidilute polyelectrolyte conductivity. The effects of the temperature, the medium, and the polymer concentration on the fractions of uncondensed counterions, the polyion conductivities, the standard state free energies of counterion association, and the coefficients of friction between the polyion and the solvent have also been investigated and the results have been interpreted from the viewpoints of polyion–counterion interactions, effective charge on the polyion, solvation of counterions and the polyionic sites, and counterion dissociation.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Polyelectrolytes are macromolecules with many ionizable groups, which in polar solvent media dissociate into a polyion and counterions of opposite charge (Dautzenberg et al., 1994; Oosawa, 1993). 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 (Schmitz, 1994).

Although the electrical conductivity has so far been measured for a great variety of polyelectrolytes (Kwak & Hayes, 1975; Kwak & Johnston, 1975; Liu, Jia, Yang, & Ji, 1999; Nagasawa, Noda, Takahashi, & Shimamoto, 1972; Rios, Barraza, & Gamboa, 1993; Rios, 2001; Szymczak, Holyk, & Ander, 1975; Tuffile & Ander, 1975; Vink, 1981; Wandrey, 1999), only a few studies reported the influence of medium and temperature on the interaction between a

polyion and its counterions derived from conductivity measurements (Abramovic & Klofutar, 1997; Barraza & Rios, 1995; Bratko & Kelbl, 1986; Hara, 1993). We have, therefore, initiated a program to investigate the behavior of different polyelectrolytes in various mixed solvent media as a function of temperature (Bhattacharai, Nandi, & Das, 2006; De & Das, 2007; Ghosh, Bhattacharai, & Das, 2009; Nandi & Das, 2005). 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 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.

2. Theory

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 (Manning, 1969, 1972, 1975). In this model, the polyion is represented by an infinitely long charged line. The small counterions

* Corresponding author. Tel.: +91 353 2776381; fax: +91 353 2699001.
E-mail address: bijan.dasus@yahoo.com (B. Das).

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 accordance with 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 (ξ) defined by (Manning, 1972, 1975)

$$\xi = \frac{e^2}{\epsilon k_B(t + 273.15)b} \quad (1)$$

where e is the protonic charge, ϵ the relative permittivity of the medium, k_B the Boltzmann constant, t the temperature in degrees Celsius 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. Following this model, the fraction of the uncondensed counterions (f) is given by

$$f = \frac{0.866}{\xi} \quad (2)$$

The molar conductivity (Λ) of polyelectrolyte solutions is given by (Manning, 1975):

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (3)$$

where λ_c^0 and λ_p are the limiting ionic molar conductivity of the counterion and the molar conductivity of the polyion at a finite concentration, respectively.

Considering the electrophoretic and relaxation contributions to the molar conductivity, Manning (1975) theoretically derived the molar conductivity of a polyion, λ_p , with counterions each bearing a charge of z_c

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

where the parameter a is the radius of the assumed rod-like polymer cylinder, while A is given by

$$A = \frac{\epsilon k_B(t + 273.15)}{3\pi\eta_0 e} \quad (5)$$

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

$$\kappa^2 = \frac{4\pi e^2 \xi^{-1} c |z_c|}{\epsilon k_B(t + 273.15)} \quad (6)$$

where c is the stoichiometric polyelectrolyte concentration in monovalent charged-groups per unit volume.

In accordance with this model, the molar conductivity (Λ) of a polyelectrolyte solution as a function of concentration is then obtained by substituting the value of λ_p from Eq. (4) into Eq. (3):

$$\Lambda = f \left[\lambda_c^0 + \frac{279A|z_c|^{-1}|\ln \kappa a|}{1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|} \right] \quad (7)$$

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 (Abramovic & Klotfutar, 1997; Barraza & Rios, 1995; Bhattarai et al., 2006; Bratko

& Kelbl, 1986; De & Das, 2007; Ghosh et al., 2009; Hara, 1993; Kwak & Hayes, 1975; Kwak & Johnston, 1975; Liu et al., 1999; Nagasawa et al., 1972; Nandi & Das, 2005; Rios et al., 1993; Rios, 2001; Szymczak et al., 1975; Tuffile & Ander, 1975; Vink, 1981; Wandrey, 1999), the concentrations are far from being very dilute and are primarily the semidilute solutions ($c > \text{overlap concentration}, c^*$) 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 (Abramovic & Klotfutar, 1997; Kwak & Hayes, 1975; Liu et al., 1999; Nandi & Das, 2005; Rios et al., 1993; Rios, 2001; Szymczak et al., 1975) 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 (Colby, Boris, Krause, & Tan, 1997) using the scaling description put forward by Dobrynin, Colby, and Rubinstein (1995) 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 $q_\xi = z_c e f g$ (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 $Q_p = N_\xi q_\xi = z_c e f g N_\xi$. 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 molar conductivity of a polyion in a semidilute solution is given by

$$\lambda_p = \frac{F z_c e f g \xi_0^2}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \quad (8)$$

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

Thus according to this model the molar conductivity of a polyelectrolyte solution as a function of concentration is given by substituting the λ_p value obtained from Eq. (8) into Eq. (3):

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

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 (Bordi, Cammetti, & Colby, 2004; Colby et al., 1997) and there has, so far, been only one report (Ghosh et al., 2009) 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

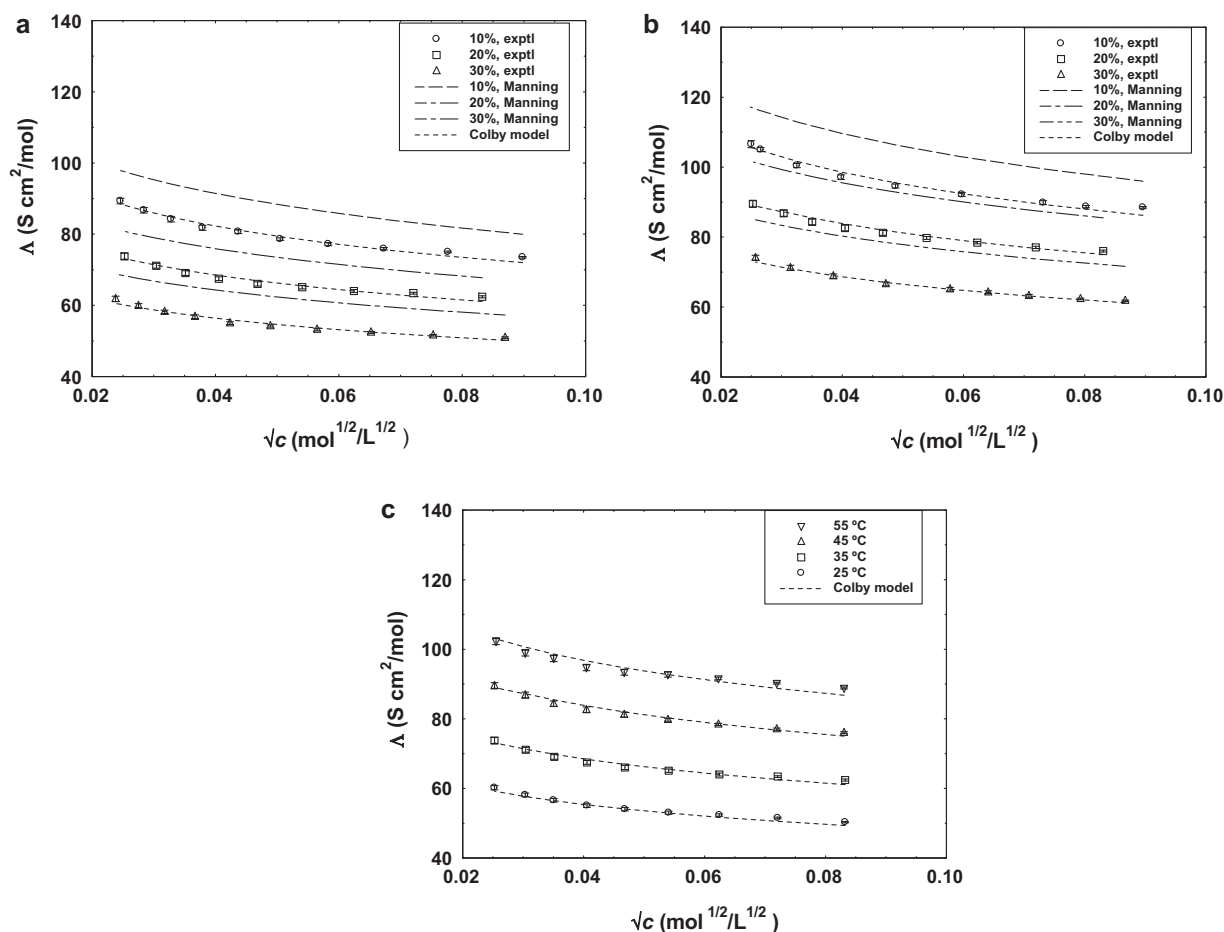


Fig. 1. Variation of the molar conductivity (Λ) of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol–water mixtures (containing 10, 20, and 30 vol.% of methanol) at 35 °C (a), at 45 °C (b), and that in a given mixed solvent medium (20 vol.% methanol) at 25, 35, 45 and 55 °C (c).

fractions of uncondensed counterions (Bordi, Colby, Cametti, Lorenzo, & Gili, 2002).

3. Experimental

3.1. 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 $10^{-6} \text{ S cm}^{-1}$ at 35 °C was used for the preparation of the solvent mixtures. 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 (Sharma, Das, Nandi, & Das, 2010).

3.2. 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 °C of the desired temperature. The details of the experimental procedure have been described earlier (Das & Hazra, 1995). 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.

3.3. Viscosity measurements

The kinematic viscosities (ν) were measured by means of a suspended level Ubbelohde viscometer in a water thermostat controlled to 0.01 °C. The kinematic viscosities were converted into the absolute viscosities (η) using the density values measured with an Anton Paar DMA 4500 M densimeter as described earlier by us (Guha & Das, 2011).

4. Results and discussion

4.1. Experimental molar conductivity

Fig. 1a and b display the variation of the molar 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 vol.% of methanol) at 35, and 45 °C respectively over the entire concentration range investigated. The representative figure (Fig. 1c), on the hand, shows the polyelectrolyte concentration dependence of the molar conductivity in a given mixed solvent medium (20 vol.%

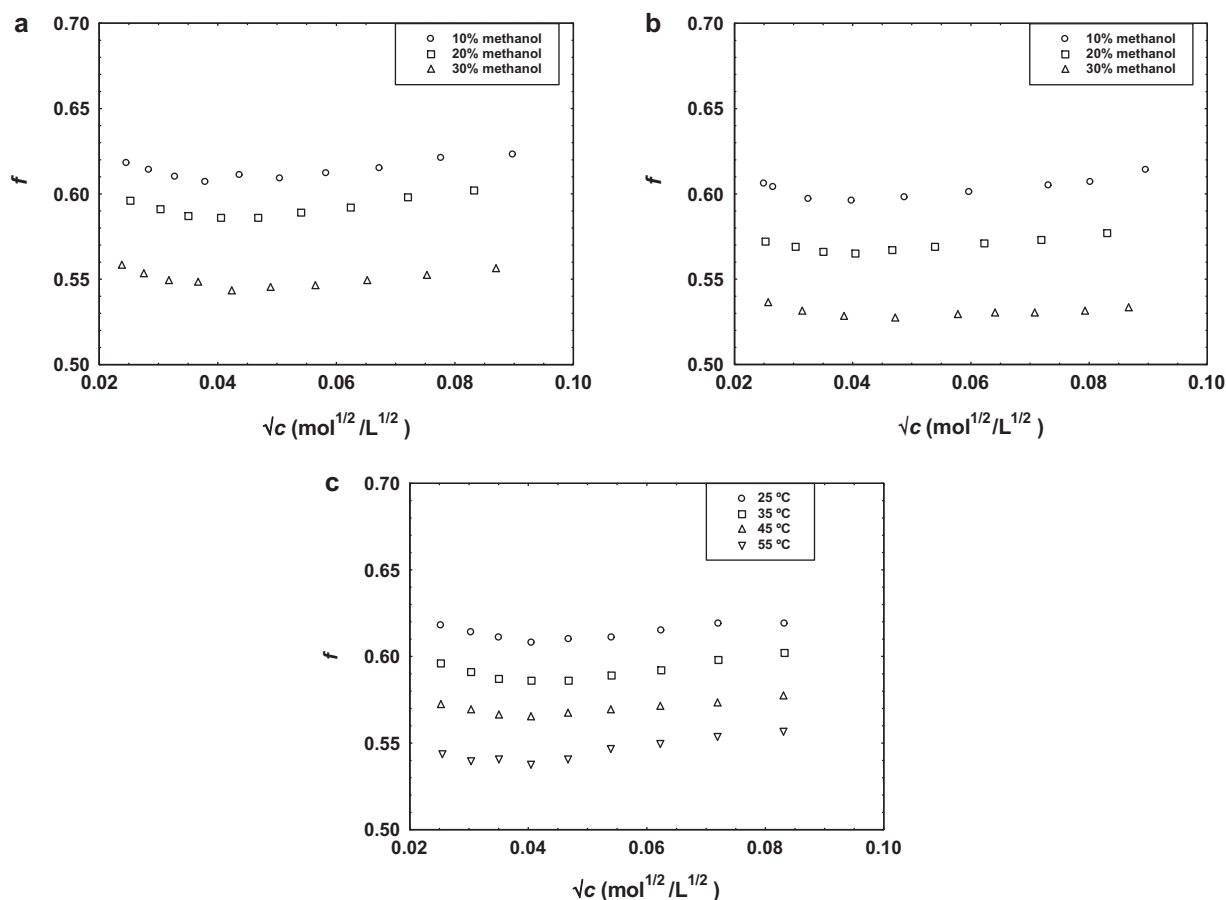


Fig. 2. Variation of the fraction of uncondensed counterions (f) of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol–water mixtures (containing 10, 20, and 30 vol.% of methanol) at 35 °C (a), at 45 °C (b), and that in a given mixed solvent medium (20 vol.% methanol) at 25, 35, 45 and 55 °C (c).

methanol) at 25, 35, 45 and 55 °C. The molar conductivities exhibit a slight increase with decreasing polymer concentration.

Figs. 1a and 2b demonstrate a decrease in the Δ values as the medium gets richer in methanol in going from 10 vol.% to 30 vol.% of methanol in methanol–water mixtures over the entire polyelectrolyte concentration range. The effect of temperature on the molar conductivity values, on the other hand, is directly evident from Fig. 1c, where in a given medium, the Δ values are found to increase as the temperature is raised from 25 to 55 °C.

4.2. Comparison with the Manning counterion condensation theory

Now we will compare the experimental Δ values with those calculated using the Manning theory. In obtaining the theoretical Δ 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 25, 35, and 45 °C have been taken from our earlier study (Bhattarai et al., 2006). For 20 vol.% methanol–water mixture at 55 °C, however, ϵ was obtained from the literature (Åkerlöf, 1932), 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 (Ghosh & Das, 2004). The values obtained are: $\eta_0 = 0.6640$ mPa s, and $\lambda_c^0 = 86.20$ S cm² mol^{−1}.

The charge density parameters ξ were calculated from Eq. (1) using the literature value for the length of the monomer unit having one charged group (Kwak & Johnston, 1975) and these are listed

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 alongwith the respective standard deviations (σ) including the standard deviations for the poor solvent correlation.

t (°C)	vol.% of methanol	ξ	f	σ (poor solvent)	σ (good solvent)
35	10	1.0321	0.61	1.49	0.93
45	10	1.0494	0.60	2.29	1.46
25	20	1.0661	0.60	0.84	0.56
35	20	1.0841	0.59	1.34	0.86
45	20	1.1041	0.57	2.51	1.55
55	20	1.1276	0.55	2.53	1.56
35	30	1.1497	0.55	0.88	0.70
45	30	1.1731	0.53	1.14	0.76

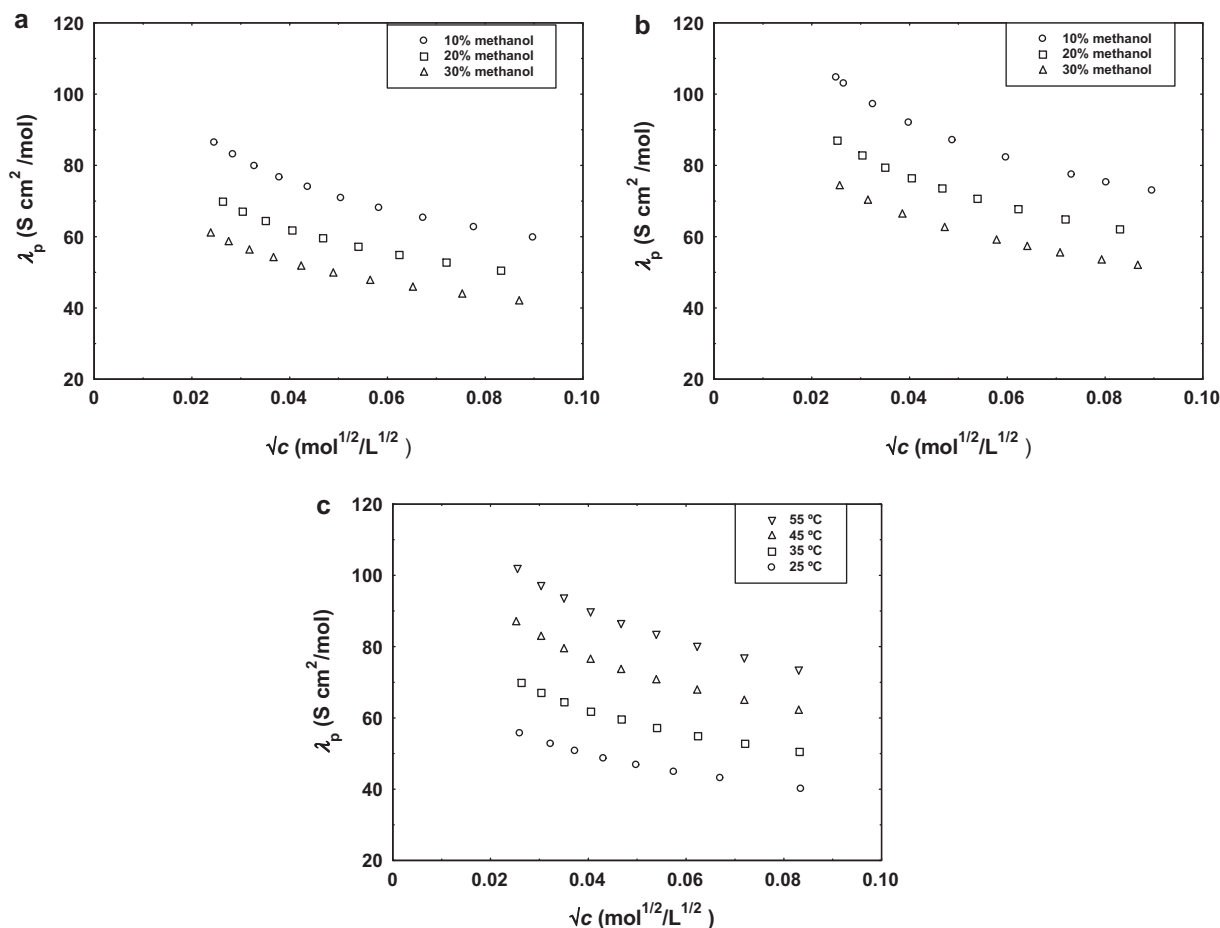


Fig. 3. Variation of the polyion molar conductivity (λ_p) of sodium carboxymethyl-cellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol–water mixtures (containing 10, 20, and 30 vol.% of methanol) at 35 °C (a), at 45 °C (b), and that in a given mixed solvent medium (20 vol.% methanol) at 25, 35, 45 and 55 °C (c).

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 Å for the present analysis (Kwak & Johnston, 1975).

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

The experimentally obtained molar 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 (Abramovic & Klofutar, 1997; Rios et al., 1993; Rios, 2001; Szymczak et al., 1975). The discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies Eq. (4).

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 (Wandrey, 1999):

$$c^* = \frac{1}{N_A L^2 b} \quad (10)$$

where N_A is the Avogadro's number and L is the contour length. 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 ($c^* \approx 0.0001 \text{ mol L}^{-1}$).

4.3. 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. (1997) 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. (8) depend upon the quality of the solvent and are, for poor solvents, given by (Colby et al., 1997)

$$\xi_e = b(\xi f^2)^{-1/3} \quad (11)$$

$$\xi_0 = (cb)^{-1/2} (\xi f^2)^{-1/3} \quad (12)$$

For good solvent cases, on the other hand, these are given by (Colby et al., 1997):

$$\xi_e = b(\xi f^2)^{-3/7} \quad (13)$$

$$\xi_0 = (cb)^{-1/2} (\xi f^2)^{-1/7} \quad (14)$$

For the present system, good solvent correlations are always found to provide a better description of the experimental results (cf. Table 1). In Fig. 1, the experimental molar conductivity values for sodium carboxymethylcellulose in methanol–water mixed solvent media in the semidilute regime have been compared with the predictions in accordance with the Colby model (dashed lines) under good solvent condition.

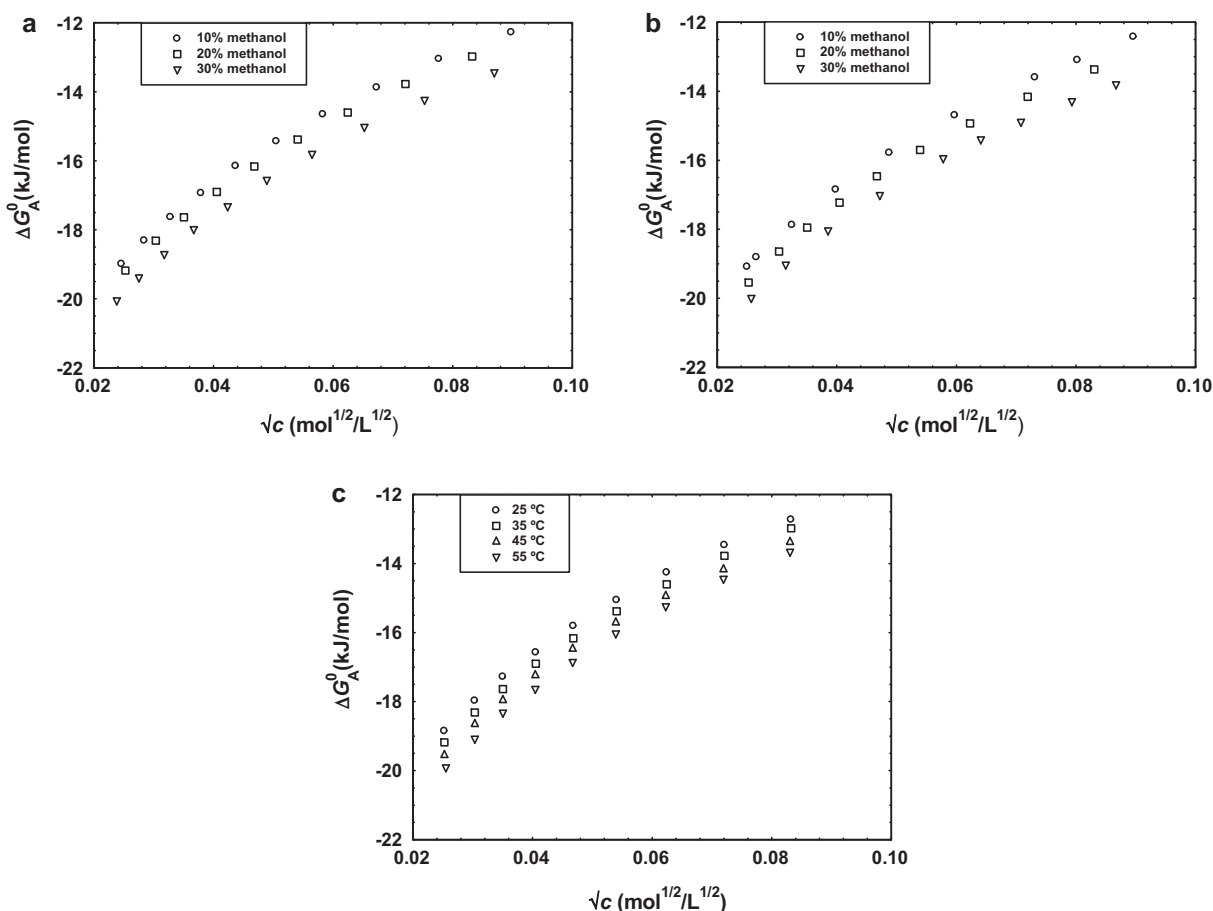


Fig. 4. Variation of the standard state free energies of counterion association (ΔG_A^0) of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol–water mixtures (containing 10, 20, and 30 vol.% of methanol) at 35 °C (a), at 45 °C (b), and that in a given mixed solvent medium (20 vol.% methanol) at 25, 35, 45 and 55 °C (c).

Fig. 1, however, reveals that although the scaling theory approach, with only one adjustable parameter – the fraction of uncondensed counterions (f) – 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 as a function of polyelectrolyte concentration from our conductivity data using Eq. (9) in conjunction with Eqs. (13), and (14). 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.

4.4. 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 (Fig. 2a and b). 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.

4.5. 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 (Chatterjee & Das, 2006). 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 (Beyer & Nordmeyer, 1995) where an increase in the charge density parameter (and hence, according

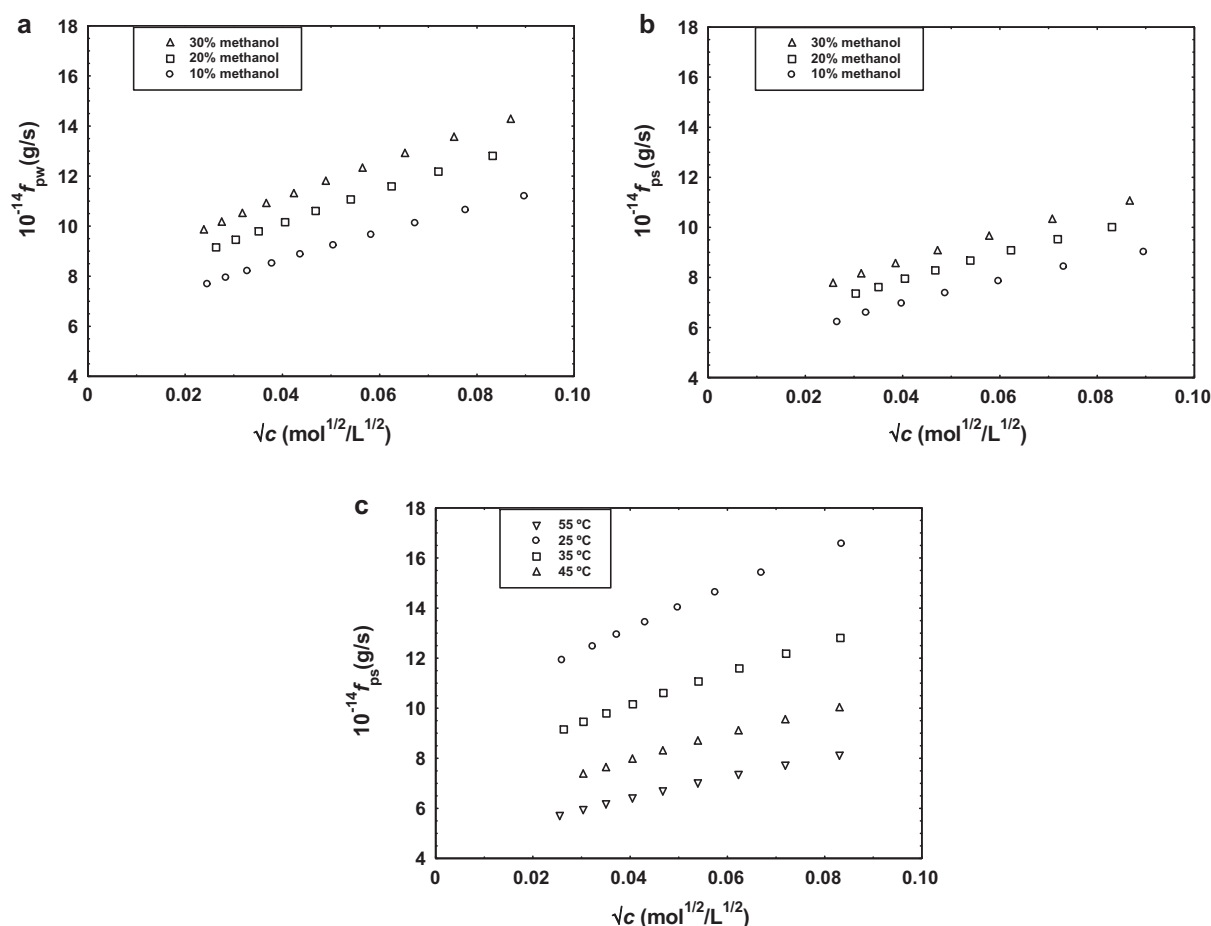


Fig. 5. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of the square root of the polyelectrolyte concentration in three different methanol–water mixtures (containing 10, 20, and 30 vol.% of methanol) at 35 °C (a), at 45 °C (b), and that in a given mixed solvent medium (20 vol.% methanol) at 25, 35, 45 and 55 °C (c).

to Eq. (1), a decrease in the fraction of uncondensed counterions) was reported with the rise of temperature. Similar results were observed with sodium carboxymethylcellulose (Nandi & Das, 2005) and sodium polystyrenesulfonate (Ghosh et al., 2009) in mixed-solvent media earlier.

4.6. Effect of medium on polyion molar conductivity

Fig. 3a and b shows that the polyion molar 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 (cf. 4.5) 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.

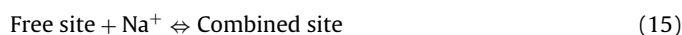
4.7. Effect of temperature on polyion molar conductivity

The polyion molar 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 molar 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 temperature increases. The present results demonstrate the predominance of the combined influence of the second and the fourth effects over that of the first and the third as far as the influence of the temperature concerned.

4.8. 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



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

$$\ln K_A = \ln \left(\frac{1-f}{f} \right) - \ln(fc) \quad (16)$$

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

$$\Delta G_A^0 = -R(t + 273.15) \ln K_A \quad (17)$$

where R is the universal gas constant.

Fig. 4a and b displays 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 vol.% of methanol at 25 and 35 °C over the entire concentration range investigated. Fig. 4c, on the hand, shows the polyelectrolyte concentration dependence of the ΔG_A^0 values in a given mixed solvent medium at different temperatures. 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 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).

4.9. 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 (Kuznestov, Stanislavskii, & Kudryavtseva, 1990):

$$f_{ps} = \frac{|z_p| f F^2}{\lambda_p} \quad (18)$$

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 Fig. 5a–c. Fig. 5a and b shows the dependence of f_{ps} on \sqrt{c} in 10, 20, and 30 mass percent methanol–water mixtures each at 25 and 35 °C. 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.

5. 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 molar 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 molar 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–counterion interactions, solvation of counterions and the polyionic sites, and counterion dissociation.

Acknowledgements

The authors gratefully acknowledge the financial support of the University of North Bengal and the Department of Science and Technology, India.

References

- Abramovic, H., & Klotfutar, C. (1997). Conductivity of some tetra-*n*-alkylammonium salts of pectic acid. *European Polymer Journal*, 33, 1295–1300.
- Åkerlöf, G. (1932). Dielectric constants of some organic solvent–water mixtures at various temperatures. *Journal of the American Chemical Society*, 54, 4125–4139.
- Barraga, R. G., & Rios, H. E. (1995). Counterion association to cationic polyelectrolytes in methanol/water mixtures. *Polymer International*, 38, 387–393.
- Beyer, P., & Nordmier, E. (1995). Some phenomena of counterion condensation on dextran sulfate. *European Polymer Journal*, 31, 1031–1036.
- Bhattacharai, A., Nandi, P., & Das, B. (2006). The effects of concentration, relative permittivity and temperature on the transport properties of sodium polystyrenesulfonate in methanol–water mixed solvent media. *Journal of Polymer Research*, 13, 475–482.
- Bordi, F., Cammetti, C., & Colby, R. H. (2004). Dielectric spectroscopy and conductivity of polyelectrolyte solutions. *Journal of Physics: Condensed Matter*, 16, R1423–R1463.
- Bordi, F., Colby, R. H., Cametti, C., Lorenzo, L. D., & Gili, T. (2002). Electrical conductivity of polyelectrolyte solutions in the semidilute and concentrated regime: The role of counterion condensation. *Journal of Physical Chemistry B*, 106, 6887–6893.
- Bratko, D., & Kelbl, A. (1986). Temperature dependence of the electrical conductivity of poly(styrenesulfonate) solutions. *Macromolecules*, 19, 2083–2085.
- Chatterjee, A., & Das, B. (2006). Electrical conductances of tetrabutylammonium bromide, sodium tetraphenylborate and sodium bromide in methanol (1) + water (2) at (298.15, 308.15, and 318.15) K. *Journal of Chemical and Engineering Data*, 51, 1352–1355.
- Colby, R. H., Boris, D. C., Krause, W. E., & Tan, J. S. (1997). Polyelectrolyte conductivity. *Journal of Polymer Science Part B: Polymer Physics*, 35, 2951–2960.
- Das, B., & Hazra, D. K. (1995). Conductometric, viscometric, and spectroscopic investigations on the solvation phenomena of alkali-metal ions and ion pairs in 2-methoxyethanol. *Journal of Physical Chemistry*, 99, 269–273.
- Dautzenberg, H., Jäger, W., Koetz, J., Philipp, B., Seidel, C., & Stscherbina, D. (1994). Polyelectrolytes. In *Formation characterization and application*. Munich: Hanser Publishers.
- De, R., & Das, B. (2007). The effects of concentration, relative permittivity and temperature on the transport properties of sodium polystyrenesulfonate in 2-ethoxyethanol–water mixed solvent media. *European Polymer Journal*, 43, 3400–3407.
- Dobrynin, A. V., Colby, R. H., & Rubinstein, M. (1995). Scaling theory of polyelectrolyte solutions. *Macromolecules*, 28, 1859–1871.

- Ghosh, D., Bhattarai, A., & Das, B. (2009). Electrical conductivity of sodium polystyrenesulfonate in acetonitrile–water mixed solvent media: Experiment and data analysis using the Manning counterion condensation model and the scaling theory approach. *Colloid and Polymer Science*, 287, 1005–1011.
- Ghosh, D., & Das, B. (2004). Electrical conductances of tetrabutylammonium bromide, sodium tetrakisphenylborate and sodium bromide in acetonitrile (1) + water (2) at (308.15, 313.15, and 318.15) K. *Journal of Chemical and Engineering Data*, 49, 1771–1776.
- Guha, C., & Das, B. (2011). Electrical conductances of sodium nitrate and ammonium nitrate in 2-methoxyethanol + water mixtures at 298.15, 308.15, 313.15, 318.15, and 323.15 K. *Journal of Molecular Liquids*, 160, 187–192.
- Hara, M. (1993). *Polyelectrolytes: Science and technology*. New York: Marcel Dekker.
- Kuznestov, I. A., Stanislavskii, O. B., & Kudryavtseva, I. S. (1990). *Russian Journal of Physical Chemistry*, 64, 1091–1094.
- Kwak, J. C. T., & Hayes, R. C. (1975). Electrical conductivity of aqueous solutions of salts of polystyrenesulfonic acid with univalent and divalent counterions. *Journal of Physical Chemistry*, 79, 265–269.
- Kwak, J. C. T., & Johnston, A. (1975). The equivalent conductivity of aqueous solutions of salts of carboxymethylcellulose: A test of Manning's limiting law. *Canadian Journal of Chemistry*, 53, 792–796.
- Liu, S., Jia, H., Yang, D., & Ji, F. (1999). Electrical conductivity and counterion association of cationic polyacrylamide derivatives in aqueous solution. *Polymer International*, 48, 1080–1084.
- Manning, G. S. (1969). Limiting laws and counterion condensation in polyelectrolyte solutions. I. Colligative properties. *Journal of Chemical Physics*, 51, 924–933.
- Manning, G. S. (1972). Polyelectrolytes. *Annual Review of Physical Chemistry*, 23, 117–140.
- Manning, G. S. (1975). A limiting law for the conductance of the rod model of a salt-free polyelectrolyte solution. *Journal of Physical Chemistry*, 79, 262–265.
- Nagasawa, M., Noda, I., Takahashi, T., & Shimamoto, N. (1972). Transport phenomena of polyelectrolytes in solution under electric field. *Journal of Physical Chemistry*, 76, 2286–2294.
- Nandi, P., & Das, B. (2005). Effects of concentration, relative permittivity and temperature on the solution behavior of sodium carboxymethylcellulose as probed by electrical conductivity. *Journal of Physical Chemistry B*, 109, 3238–3242.
- Oosawa, F. (1993). *Polyelectrolytes*. New York: Marcel Dekker.
- Rios, H. E. (2001). Electrical conductivity properties of poly[(maleic acid)-co-(vinyl pyrrolidone)] salts in aqueous solutions. *Polymer International*, 50, 885–890.
- Rios, H. E., Barraza, R. G., & Gamboa, I. C. (1993). Polyelectrolyte solutions. Electrical conductivity and counterion condensation. *Polymer International*, 31, 213–217.
- Schmitz, K. S. (1994). *Macro-ion characterization from dilute solutions to complex fluids*, PTACS symposium series 548. Washington, DC: American Chemical Society.
- Sharma, R., Das, B., Nandi, P., & Das, C. (2010). Viscosity of sodium carboxymethylcellulose in ethylene glycol–water mixed solvent media: Separation of the influences of polyion conformation and electrostatic interactions on the reduced viscosity. *Journal of Polymer Science Part B: Polymer Physics*, 48, 1196–1202.
- Szymczak, J., Holyk, P., & Ander, P. (1975). Electrical conductivity of aqueous solutions of monovalent salts of polystyrenesulfonate. *Journal of Physical Chemistry*, 79, 269–272.
- Tuffile, F. M., & Ander, P. (1975). Electric transport for aqueous solutions of sodium alginate and sodium polygalacturonate. *Macromolecules*, 8, 789–792.
- Vink, H. (1981). Conductivity of polyelectrolytes in very dilute solutions. *Journal of the Chemical Society, Faraday Transactions I*, 77, 2439–2499.
- Wandrey, C. (1999). Concentration regimes in polyelectrolyte solutions. *Langmuir*, 15, 4069–4075.