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# Polyion–counterion interactions in sodium carboxymethylcellulose–ethylene glycol–water ternary solutions

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ABSTRACT

Polyion–counterion interactions in sodium carboxymethylcellulose–ethylene glycol–water ternary system have been investigated with special reference to their variations with the polyelectrolyte concentration, the medium relative permittivity and the temperature using electrical conductance measurements. The experimental data have been analyzed on the basis of a model for semidilute polyelectrolyte conductivity which takes into account the scaling arguments proposed by Dobrynin et al. Concentration-dependent moderate counterion condensation (24–33%) was observed. Counterion condensation is found to be spontaneous which depends upon the EG-content of the medium and the temperature. A major proportion of the current is transported by the carboxymethylcellulose polyions. The results further demonstrated that the monomer units experience more frictional resistance in solution as the EG-content increases or as the temperature decreases.

## 1. Introduction

Polyelectrolytes are macromolecules with a large number of ionizable groups, which in polar solvent media dissociate into a polyion and counterions of opposite charge (Dautzenberg et al., 1994; Oosawa, 1993). Current interest in charged polymer solutions stems from the needs to understand the behavior of biopolymers since they are charged under physiological conditions and many of their biological functions are governed by their polyelectrolyte behavior (Schmitz, 1994). The interactions between the polyion and counterions mainly control the thermodynamic and transport properties of polyelectrolytes in solutions. Now, the transport properties of polyelectrolyte solutions, obtained by measuring their electrical conductivities, can be conveniently exploited to unravel the solution behavior of polyelectrolytes because electrical conductivity takes into account the movement of any charged species present in the system under the influence of an externally applied electric field.

Although the electrical conductivity has, so far, been measured for a great variety of polyelectrolytes (Kwak & Hayes, 1975; Kwak & Johnston, 1975; Kwak, Murphy, & Spiro, 1978; Liu, Jia, Yang, & Ji, 1999; Nagasawa, Noda, Takahashi, & Shimamoto, 1972; Rios, 2001; Rios, Barraza, & Gamboa, 1993; Szymczak, Holyk, & Ander, 1975; Tuffile & Ander, 1975; Vink, 1981; Wandrey, 1999), only a handful of such studies paid attention to the influence of medium and temperature on the interaction between a polyion and its counterions (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 with a view to obtain a comprehensive information on polyion–counterion interactions (Bhattarai, Nandi, & Das, 2006; Chatterjee, Das, & Das, 2011; De & Das, 2007; Ghosh, Bhattarai, & Das, 2009; Nandi & Das, 2005). The present communication deals with a study on the electrical conductivity of the semidilute solutions of NaCMC in EG–water mixed solvent media at different temperatures and the data have been analyzed on the basis of a model derived from the scaling picture for the configuration of polyions (Dobrynin, Colby, & Rubinstein, 1995). The objective of this contribution is to examine the influences of the polymer concentration, the temperature and the medium on a multitude of parameters, specifically (*i*) the fractions of uncondensed counterions, (*ii*) the polyion equivalent conductivities, (*iii*) the standard state free energies of counterion condensation, (*iv*) the polyion transference numbers, and (*v*) the solvodynamic friction coefficients of the polyion in the solution to provide as complete picture as possible for the polyion–counterion interactions as well as of the counterion condensation phenomena in polyelectrolyte solutions. The results are discussed from the viewpoint of the general solution behavior of polyelectrolytes.

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## 2. Theory

The description of different electrical properties of polyelectrolytes in solutions and of the polyion–counterion interactions is generally based on the Manning counterion condensation theory (Manning, 1969, 1972, 1975, 1981). Within the premises of this model, a 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 they interact with the charged polyions through purely Coulombic forces, so that the screening effect extends over the Debye length. The uncondensed mobile counterions are treated in terms of the Debye–Hückel approximation. The solvent is assumed to be a dielectric continuum characterized by a spatially uniform relative permittivity $\varepsilon$. Interactions among the polyions are neglected, the theory being addressed to highly diluted solutions.

However, the failure of this theory in describing the conductivity behavior of polyelectrolyte solutions is now well known, and could be ascribed to various unrealistic assumptions underlying this model (Abramovic & Klofutar, 1997; Kwak & Hayes, 1975; Liu et al., 1999; Nandi & Das, 2005; Rios, 2001; Rios et al., 1993; Szymczak et al., 1975). Majority of the experimental results described in the literature seem to have covered the semidilute concentration regimes, and in the case of semidilute polyelectrolyte solutions, 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 later proposed by Colby et al. (1997) using the scaling description put forward by Dobrynin et al. (1995) for the configuration of a polyion chain. Following this model, in semidilute solutions, the polyion chain is modeled as a random walk of $N_\xi$ correlation blobs of size $\xi_0$, each of them containing $g$ monomers. Each blob bears an electric charge $q_\xi = z_c efg$ ($z_c$ 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 $Q_p = N_\xi q_\xi = z_c efgN_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of $g_e$ electrostatic blobs of size $\xi_e$. This means that for length scales less than $\xi_0$, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size $\xi_e$), and for length scales greater than $\xi_0$, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size $\xi_0$.

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

$$\lambda_p = \frac{Fz_c efc\xi_0^2}{3\pi\eta_0} \ln\left(\frac{\xi_0}{\xi_e}\right) \tag{1}$$

where $F$ is the Faraday number, $c$ is the number of monovalently-charged groups per cm$^3$ and the other symbols have their usual significance.

Thus, following this model the equivalent conductivity of a polyelectrolyte solution as a function of concentration is given by (Colby et al., 1997) by the following equation:

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

where $\lambda_c^0$ is the limiting equivalent conductivity of the counterion.

Within this model, the parameter $f$ – that defines the fraction of uncondensed counterions – has been treated as an adjustable quantity and could be quantified from experiments in conjunction with this new approach. This new model has been applied, so far, to a limited number of aqueous polyelectrolytes (Bordi, Cammetti, & Colby, 2004; Bordi, Colby, Cametti, Lorenzo, & Gili, 2002) and there has, so far, been only a couple of reports (Chatterjee et al., 2011; Ghosh et al., 2009) by our group on the application of this model to polyelectrolytes 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 (Bordi et al., 2002).

Because of the limited solubility of the polyeletrolytes, however, we had to confine ourselves within a narrow composition range of the mixed solvent media in the earlier studies. Here, we have been fortunate enough to cover a wide composition range of the media, courtesy good solubility of the investigated polyelectrolyte in EG–water mixtures.

## 3. Experimental

### 3.1. Materials

EG (E. Merck, India, 99.9% pure) was dried over molecular sieves and fractionally distilled. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance of less than $10^{-6}$ S cm$^{-1}$ at 30 °C was used for the preparation of the solvent mixtures. The physical properties of EG–water mixtures used in this study at 30, 35, and 45 °C, namely the coefficients of viscosity ($\eta_0$), and the relative permittivities ($\varepsilon$), are reported in Table 1. Also included in this table are the limiting equivalent conductivities of the counterion (Na$^+$), $\lambda_c^0$ in EG–water mixtures containing 0, 10, 20, 30, 50 and 70 mass% of EG taken from the literature (Sharma, Das, Chatterjee, & Das, 2009).

NaCMC employed in this investigation was purchased from Aldrich Chemical Company, Inc. The sample had a weight-average molecular weight of 90,000 and a degree of substitution of 0.7. It was characterized as described earlier by us (Sharma, Das, Nandi, & Das, 2010).

### 3.2. Conductance measurements

Conductance measurements were carried out on an Orion 3-Star 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

**Table 1**
Physical properties of EG–water mixtures, and the corresponding $\lambda_c^0$ values of sodium ion.

| $t$ (°C) | Mass % of EG | Coefficient of viscosity (mPa s) | Relative permittivity | $\lambda_c^0$ (S cm$^2$/mol) |
|---|---|---|---|---|
| 30 | 0 | 0.798 | 76.55 | 55.72 |
| 35 | 0 | 0.719 | 74.82 | 61.54 |
| 45 | 0 | 0.596 | 71.51 | 73.26 |
| 30 | 10 | 1.152 | 75.65 | 42.93 |
| 35 | 10 | 0.908 | 72.07 | 52.59 |
| 45 | 10 | 0.738 | 68.68 | 64.12 |
| 30 | 20 | 1.469 | 72.68 | 34.65 |
| 35 | 20 | 1.149 | 69.47 | 42.87 |
| 45 | 20 | 0.924 | 66.27 | 53.01 |
| 30 | 30 | 1.903 | 69.77 | 29.19 |
| 35 | 30 | 1.462 | 66.30 | 36.75 |
| 45 | 30 | 1.164 | 63.00 | 45.81 |
| 30 | 50 | 2.832 | 61.62 | 19.88 |
| 35 | 50 | 2.436 | 60.12 | 25.14 |
| 45 | 50 | 1.876 | 57.12 | 31.35 |
| 30 | 70 | 4.955 | 53.06 | 11.50 |
| 35 | 70 | 4.185 | 51.83 | 15.50 |
| 45 | 70 | 3.101 | 49.27 | 20.04 |

in a water bath maintained within ±0.05 °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 ($\kappa_0$) from those of the polyelectrolyte solutions ($\kappa$).

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

## 4. Results and discussion

### 4.1. Experimental equivalent conductivity

Table 3 lists the equivalent conductivity of NaCMC ($\Lambda$) solutions as a function of the square root of the polyelectrolyte concentration expressed in equivalents of monovalently-charged groups per liter ($c_p$) in six different EG–water mixtures (containing 0, 10, 20, 30, 50 and 70 mass% of EG) at 30, 35 and 45 °C. In Fig. 1(a) is displayed the variation of $\Lambda$ as a function of the square root of $c_p$ in EG–water mixtures at 35 °C over the entire concentration range investigated. The representative plot, Fig. 1(b), on the other hand, shows the polyelectrolyte concentration dependence of the equivalent conductivity at a given mass percent of EG (30 mass%) at 30, 35, and 45 °C. The equivalent conductivities exhibit a slight increase with decreasing polymer concentration.

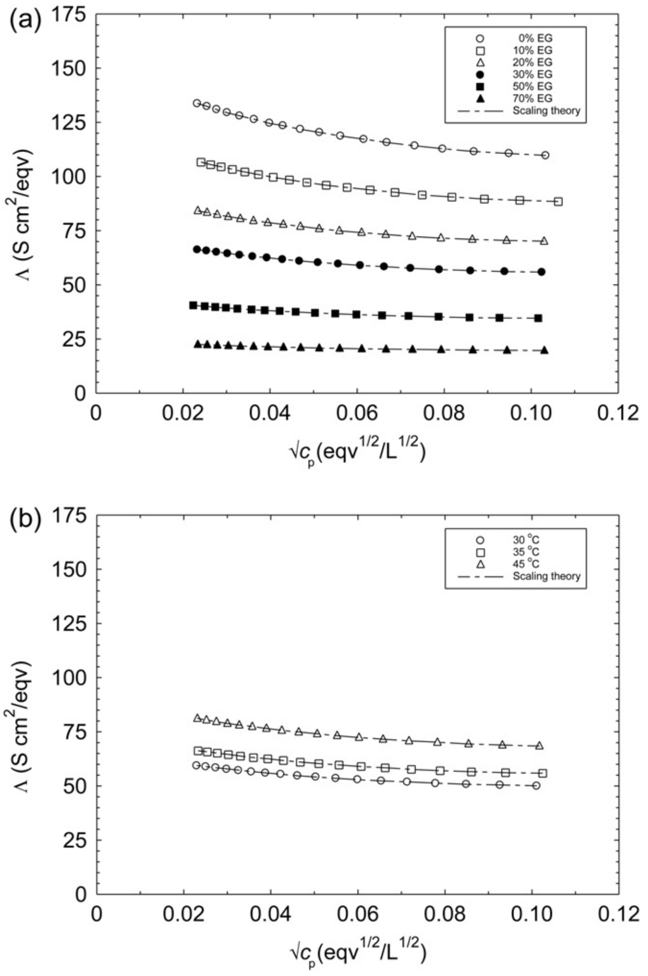

**Fig. 1.** (a) Concentration dependence of the equivalent conductivities ($\Lambda$) of NaCMC in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% of EG) at 35 °C, along with the predicted values according to scaling theory using good solvent correlation. (b) Concentration dependence of the equivalent conductivities ($\Lambda$) of NaCMC in EG–water mixed solvent media containing 30 mass% of EG at 30, 35, and 45 °C, along with the predicted values according to scaling theory using good solvent correlation.

Table 3 and Fig. 1(a) demonstrated a decrease in the $\Lambda$ values as the medium gets richer in EG in going from 0 mass% to 70 mass% of EG in EG–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. 1(b). At a given mass percent of EG, the $\Lambda$ values are found to increase with increase in temperature.

### 4.2. Scaling theory and the fractions of uncondensed counterions

Analysis of the conductivity data on the basis of the scaling theory approach requires information on the electrostatic blob size ($\xi_e$) and the correlation blob size ($\xi_0$) appearing in Eq. (1). These two quantities depend upon the quality of the solvent and are, for poor solvents, given by (Colby et al., 1997)

$$\xi_e = b\left(\frac{A^2}{\xi}\right)^{1/3} \tag{3}$$

$$\xi_0 = (cb)^{-1/2}\left(\frac{A^2}{\xi}\right)^{1/3} \tag{4}$$

where $\xi$ is the linear charge density parameter defined by (Manning, 1972, 1975)

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

where $e$ is the protonic charge, $\varepsilon$ the relative permittivity of the medium, $k_B$ the Boltzmann constant and $T$ the absolute temperature and $b$ the contour distance per unit charge on the polyion chain.

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

$$\xi_e = b\left(\frac{A^2}{\xi}\right)^{3/7} \tag{6}$$

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

For the present system, however, good solvent correlations are always found to provide a better description of the experimental results. Table 2 lists the fractions of uncondensed counterions ($f$) for the best-fit of the experimental equivalent conductances for NaCMC in EG–water mixed solvent media following the scaling theory approach using good solvent correlation along with the respective standard deviations ($\sigma$).

It is worth noting that although the scaling theory approach, with only one adjustable parameter (the fraction of uncondensed counterions, $f$) provides a very good fit of the experimental results over the entire concentration range a quantitative description is, however, yet to be achieved. The present analyses 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. (2) in conjunction with Eqs. (6) and (7). The concentration dependence of $f$ thus obtained is shown in Table 3. Some of the results are depicted graphically in the representative Fig. 2(a) and (b). The polyion equivalent conductivities have also been computed on the basis of these $f$ values and some selected results are shown in Fig. 3(a) and (b).

**Table 2**
The fractions of uncondensed counterions ($f$) for the best-fit of the experimental equivalent conductances for NaCMC in EG–water mixed solvent media following the scaling theory approach using good solvent correlation along with the respective standard deviations ($\sigma$).

| $t$ (°C) | Mass % of EG | $f$ | $\sigma$ |
|---|---|---|---|
| 30 | 0 | 0.76 | 1.9 |
| 35 | 0 | 0.76 | 2.1 |
| 45 | 0 | 0.74 | 2.6 |
| 30 | 10 | 0.76 | 1.6 |
| 35 | 10 | 0.75 | 1.7 |
| 45 | 10 | 0.73 | 2.2 |
| 30 | 20 | 0.76 | 1.5 |
| 35 | 20 | 0.74 | 1.3 |
| 45 | 20 | 0.73 | 1.5 |
| 30 | 30 | 0.74 | 0.9 |
| 35 | 30 | 0.73 | 1.0 |
| 45 | 30 | 0.72 | 1.3 |
| 30 | 50 | 0.72 | 0.6 |
| 35 | 50 | 0.71 | 0.7 |
| 45 | 50 | 0.70 | 0.9 |
| 30 | 70 | 0.70 | 0.3 |
| 35 | 70 | 0.69 | 0.5 |
| 45 | 70 | 0.67 | 0.6 |

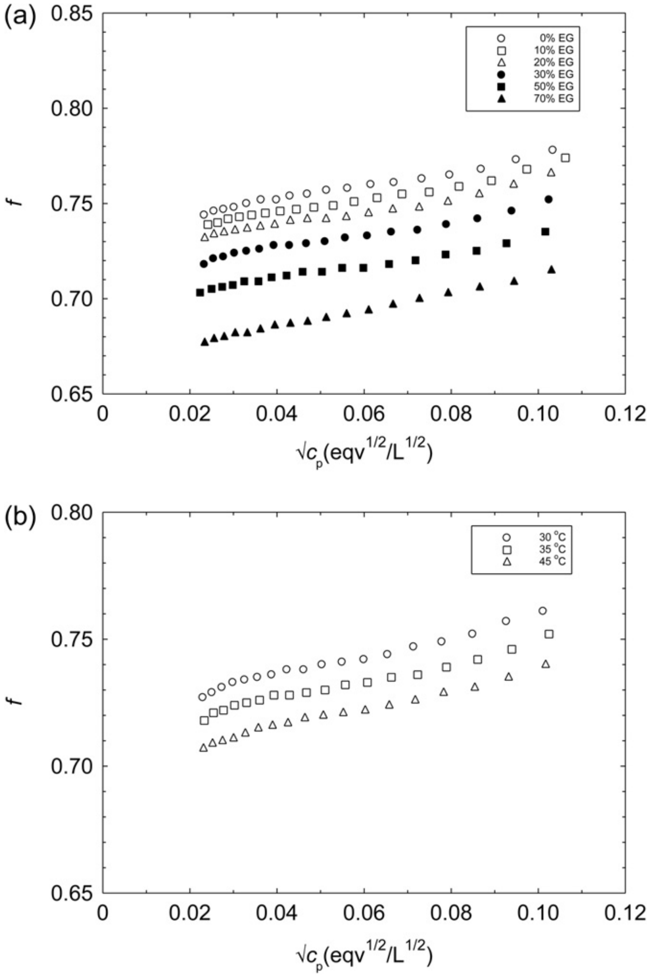

**Fig. 2.** (a) Concentration dependence of the fractions of uncondensed counterions ($f$) for NaCMC in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% of EG) at 35 °C. (b) Concentration dependence of the fractions of uncondensed counterions ($f$) for NaCMC in EG–water mixed solvent media containing 30 mass% of EG at 30, 35, and 45 °C.

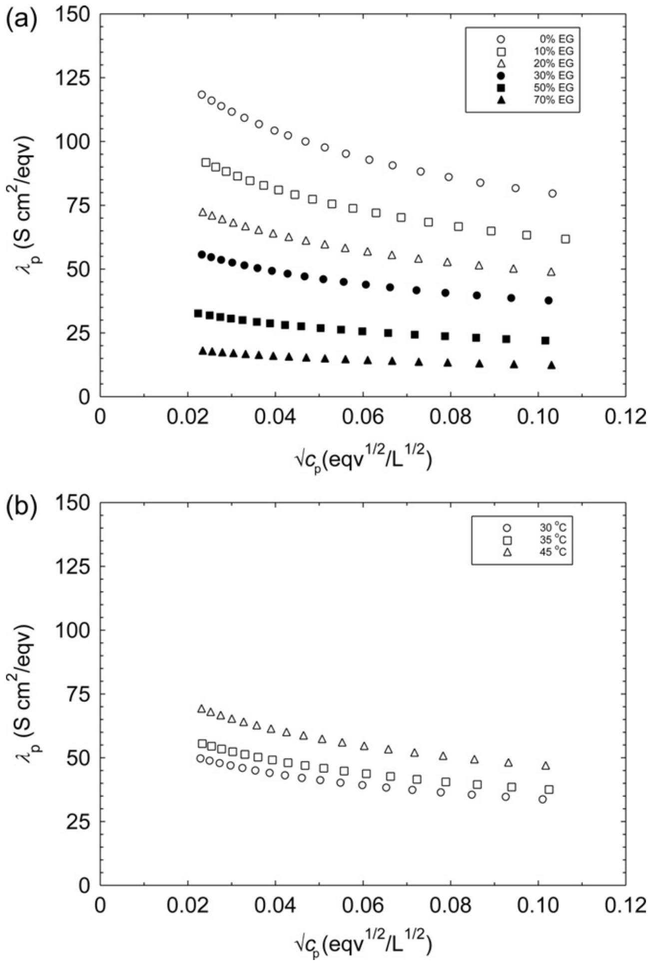

**Fig. 3.** (a) Concentration dependence of the polyion equivalent conductivities ($\lambda_p$) in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% of EG) at 35 °C. (b) Concentration dependence of the polyion equivalent conductivities ($\lambda_p$) in EG–water mixed solvent media containing 30 mass% of EG at 30, 35, and 45 °C.

Table 3 along with Fig. 2(a) and (b) 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 minor proportion (22–34%) of the counterions get condensed onto the polyion chains.

### *4.3. Effect of polyelectrolyte concentration on counterion condensation*

From Table 3 and Fig. 2(a) and (b) one observes that the fractions of the uncondensed counterions increase as polyelectrolyte concentration increases at a given temperature in a given solvent medium. As polyelectrolyte concentration increases, the relative permittivity of the medium is known to increase, owing to the polarizability of polyelectrolytes (Oosawa, 1993). While the increase in the effective relative permittivity of the medium is not completely understood yet (Mohanty & Zhao, 1996), the experimental evidence is well established (Cleland, 1991; Oosawa, 1993). The increase in the relative permittivity of the medium ($\varepsilon$) would result in a decrease in the Bjerrum length ($l_B = e^2/\varepsilon kT$). Since the Bjerrum length sets the scale for the distance between the dissociated counterions on the polyion chain (Manning, 1969, 1996; Oosawa, 1993), there will be fewer condensed counterions as the relative permittivity of the medium increases.

**Table 3**
Concentration dependence of the equivalent conductances ($\Lambda$) and the calculated fractions of uncondensed counterions ($f$) for NaCMC following the scaling theory approach using good solvent correlation in water and EG–water mixed solvent media.

| $t = 30\,^{\circ}\mathrm{C}$ | | | $t = 35\,^{\circ}\mathrm{C}$ | | | $t = 45\,^{\circ}\mathrm{C}$ | | |
|---|---|---|---|---|---|---|---|---|
| $\sqrt{c_p}$ | $\Lambda$ | $f$ | $\sqrt{c_p}$ | $\Lambda$ | $f$ | $\sqrt{c_p}$ | $\Lambda$ | $f$ |
| NaCMC in water | | | | | | | | |
| 0.10575 | 99.79 | 0.784 | 0.10336 | 109.67 | 0.778 | 0.10689 | 127.67 | 0.765 |
| 0.09692 | 100.34 | 0.777 | 0.09495 | 110.62 | 0.773 | 0.09808 | 128.41 | 0.759 |
| 0.08883 | 101.36 | 0.773 | 0.0869 | 111.48 | 0.768 | 0.09008 | 129.78 | 0.756 |
| 0.08141 | 102.35 | 0.769 | 0.07968 | 112.73 | 0.765 | 0.08190 | 131.27 | 0.752 |
| 0.07461 | 103.56 | 0.767 | 0.07328 | 114.15 | 0.763 | 0.07527 | 133.21 | 0.751 |
| 0.06838 | 104.64 | 0.764 | 0.06687 | 115.67 | 0.761 | 0.06931 | 134.54 | 0.748 |
| 0.06268 | 105.89 | 0.761 | 0.06156 | 117.14 | 0.760 | 0.06356 | 136.19 | 0.746 |
| 0.05734 | 107.25 | 0.760 | 0.05619 | 118.71 | 0.758 | 0.05778 | 138.06 | 0.744 |
| 0.05250 | 108.69 | 0.758 | 0.05138 | 120.34 | 0.757 | 0.05316 | 139.81 | 0.743 |
| 0.04807 | 110.19 | 0.758 | 0.04697 | 121.82 | 0.755 | 0.04894 | 141.45 | 0.742 |
| 0.04432 | 111.55 | 0.757 | 0.04297 | 123.45 | 0.754 | 0.04475 | 143.17 | 0.740 |
| 0.04032 | 113.10 | 0.755 | 0.03988 | 124.63 | 0.752 | 0.04120 | 145.14 | 0.740 |
| 0.03701 | 114.67 | 0.755 | 0.03635 | 126.40 | 0.752 | 0.03745 | 146.76 | 0.737 |
| 0.03391 | 116.11 | 0.754 | 0.03301 | 127.99 | 0.750 | 0.03457 | 148.44 | 0.736 |
| 0.03148 | 117.26 | 0.753 | 0.03014 | 129.48 | 0.748 | 0.02904 | 151.41 | 0.732 |
| 0.02860 | 118.89 | 0.752 | 0.02773 | 130.98 | 0.747 | 0.02639 | 153.44 | 0.731 |
| 0.02639 | 120.04 | 0.751 | 0.02551 | 132.35 | 0.746 | 0.02417 | 155.03 | 0.729 |
| | | | 0.02329 | 133.65 | 0.744 | | | |
| NaCMC in 10% EG–water | | | | | | | | |
| 0.10653 | 80.59 | 0.781 | 0.10623 | 88.42 | 0.774 | 0.10853 | 105.37 | 0.761 |
| 0.09764 | 81.05 | 0.775 | 0.09736 | 89.05 | 0.768 | 0.09947 | 105.99 | 0.755 |
| 0.08949 | 81.60 | 0.770 | 0.08923 | 89.60 | 0.762 | 0.09116 | 106.81 | 0.750 |
| 0.08201 | 82.30 | 0.765 | 0.08178 | 90.49 | 0.759 | 0.08355 | 108.10 | 0.748 |
| 0.07517 | 83.23 | 0.763 | 0.07496 | 91.43 | 0.756 | 0.07658 | 109.23 | 0.745 |
| 0.06889 | 84.03 | 0.760 | 0.06870 | 92.65 | 0.755 | 0.07018 | 110.59 | 0.743 |
| 0.06314 | 85.14 | 0.758 | 0.06296 | 93.75 | 0.753 | 0.06433 | 111.91 | 0.741 |
| 0.05787 | 86.08 | 0.756 | 0.05771 | 94.91 | 0.751 | 0.05895 | 113.26 | 0.739 |
| 0.05304 | 87.11 | 0.755 | 0.05289 | 95.97 | 0.749 | 0.05403 | 114.67 | 0.738 |
| 0.04861 | 88.29 | 0.754 | 0.04847 | 97.20 | 0.748 | 0.04952 | 115.98 | 0.736 |
| 0.04455 | 89.41 | 0.753 | 0.04443 | 98.42 | 0.747 | 0.04539 | 117.38 | 0.735 |
| 0.04083 | 90.51 | 0.752 | 0.04072 | 99.66 | 0.746 | 0.04160 | 118.72 | 0.733 |
| 0.03742 | 91.57 | 0.751 | 0.03732 | 100.89 | 0.745 | 0.03813 | 120.03 | 0.732 |
| 0.03430 | 92.63 | 0.749 | 0.03420 | 102.08 | 0.744 | 0.03494 | 121.36 | 0.730 |
| 0.03144 | 93.81 | 0.749 | 0.03135 | 103.26 | 0.743 | 0.02935 | 123.89 | 0.727 |
| 0.02881 | 94.93 | 0.748 | 0.02873 | 104.47 | 0.742 | 0.02690 | 125.21 | 0.725 |
| 0.02641 | 95.94 | 0.747 | 0.02633 | 105.42 | 0.740 | 0.02466 | 126.31 | 0.723 |
| 0.02420 | 96.99 | 0.745 | 0.02413 | 106.62 | 0.739 | | | |
| NaCMC in 20% EG–water | | | | | | | | |
| 0.10437 | 62.97 | 0.773 | 0.10295 | 70.10 | 0.766 | 0.10292 | 84.61 | 0.751 |
| 0.09566 | 63.40 | 0.768 | 0.09435 | 70.47 | 0.760 | 0.09433 | 85.14 | 0.746 |
| 0.08767 | 63.96 | 0.764 | 0.08648 | 70.99 | 0.755 | 0.08645 | 85.93 | 0.742 |
| 0.08035 | 64.48 | 0.760 | 0.07926 | 71.60 | 0.751 | 0.07923 | 86.88 | 0.740 |
| 0.07364 | 65.20 | 0.757 | 0.07264 | 72.34 | 0.748 | 0.07262 | 87.93 | 0.738 |
| 0.06750 | 65.90 | 0.755 | 0.06658 | 73.21 | 0.747 | 0.06656 | 88.84 | 0.735 |
| 0.06186 | 66.66 | 0.753 | 0.06102 | 74.13 | 0.745 | 0.06100 | 89.91 | 0.734 |
| 0.05670 | 67.56 | 0.752 | 0.05592 | 74.94 | 0.743 | 0.05591 | 90.92 | 0.732 |
| 0.05196 | 68.37 | 0.751 | 0.05126 | 75.93 | 0.742 | 0.05124 | 92.04 | 0.731 |
| 0.04763 | 69.13 | 0.749 | 0.04698 | 76.96 | 0.742 | 0.04696 | 93.09 | 0.729 |
| 0.04365 | 70.00 | 0.748 | 0.04305 | 77.90 | 0.741 | 0.04304 | 94.39 | 0.729 |
| 0.04001 | 70.80 | 0.747 | 0.03946 | 78.71 | 0.739 | 0.03945 | 95.43 | 0.727 |
| 0.03667 | 71.65 | 0.746 | 0.03617 | 79.61 | 0.738 | 0.03616 | 96.41 | 0.726 |
| 0.03360 | 72.51 | 0.745 | 0.03315 | 80.55 | 0.737 | 0.03314 | 97.54 | 0.725 |
| 0.03080 | 73.28 | 0.744 | 0.03038 | 81.48 | 0.736 | 0.03037 | 98.55 | 0.723 |
| 0.02823 | 74.01 | 0.742 | 0.02784 | 82.43 | 0.735 | 0.02783 | 99.67 | 0.722 |
| 0.02587 | 74.92 | 0.742 | 0.02552 | 83.40 | 0.734 | 0.02551 | 100.55 | 0.720 |
| 0.02371 | 75.67 | 0.740 | 0.02339 | 84.14 | 0.732 | 0.02338 | 101.61 | 0.719 |
| NaCMC in 30% EG–water | | | | | | | | |
| 0.10113 | 50.01 | 0.761 | 0.10248 | 55.82 | 0.752 | 0.10170 | 68.37 | 0.740 |
| 0.09268 | 50.38 | 0.757 | 0.09393 | 56.13 | 0.746 | 0.09321 | 68.81 | 0.735 |
| 0.08495 | 50.77 | 0.752 | 0.08608 | 56.49 | 0.742 | 0.08542 | 69.39 | 0.731 |
| 0.07786 | 51.19 | 0.749 | 0.07890 | 57.02 | 0.739 | 0.07829 | 70.08 | 0.729 |
| 0.07136 | 51.82 | 0.747 | 0.07231 | 57.62 | 0.736 | 0.07176 | 70.79 | 0.726 |
| 0.06540 | 52.31 | 0.744 | 0.06627 | 58.32 | 0.735 | 0.06577 | 71.55 | 0.724 |
| 0.05994 | 52.89 | 0.742 | 0.06074 | 58.98 | 0.733 | 0.06028 | 72.36 | 0.722 |
| 0.05493 | 53.52 | 0.741 | 0.05567 | 59.65 | 0.732 | 0.05524 | 73.22 | 0.721 |
| 0.05035 | 54.15 | 0.740 | 0.05102 | 60.26 | 0.730 | 0.05063 | 74.06 | 0.720 |
| 0.04615 | 54.71 | 0.738 | 0.04676 | 60.99 | 0.729 | 0.04640 | 74.89 | 0.719 |
| 0.04229 | 55.39 | 0.738 | 0.04286 | 61.73 | 0.728 | 0.04253 | 75.65 | 0.717 |
| 0.03876 | 55.98 | 0.736 | 0.03928 | 62.47 | 0.728 | 0.03898 | 76.54 | 0.716 |

Table 3 (*Continued*)

| $t = 30\,^{\circ}\mathrm{C}$ | | | $t = 35\,^{\circ}\mathrm{C}$ | | | $t = 45\,^{\circ}\mathrm{C}$ | | |
|---|---|---|---|---|---|---|---|---|
| $\sqrt{c_p}$ | $\Lambda$ | $f$ | $\sqrt{c_p}$ | $\Lambda$ | $f$ | $\sqrt{c_p}$ | $\Lambda$ | $f$ |
| 0.03553 | 56.56 | 0.735 | 0.03600 | 63.08 | 0.726 | 0.03573 | 77.33 | 0.715 |
| 0.03256 | 57.18 | 0.734 | 0.03300 | 63.78 | 0.725 | 0.03274 | 78.07 | 0.713 |
| 0.02984 | 57.81 | 0.733 | 0.03024 | 64.46 | 0.724 | 0.03001 | 78.85 | 0.711 |
| 0.02735 | 58.38 | 0.731 | 0.02772 | 65.11 | 0.722 | 0.02750 | 79.67 | 0.710 |
| 0.02507 | 58.86 | 0.729 | 0.02540 | 65.71 | 0.721 | 0.02521 | 80.45 | 0.709 |
| 0.02297 | 59.37 | 0.727 | 0.02328 | 66.20 | 0.718 | 0.02310 | 81.13 | 0.707 |
| NaCMC in 50% EG–water | | | | | | | | |
| 0.10314 | 29.05 | 0.749 | 0.10171 | 34.45 | 0.735 | 0.10271 | 42.86 | 0.724 |
| 0.09474 | 29.22 | 0.745 | 0.09278 | 34.62 | 0.729 | 0.09401 | 43.07 | 0.719 |
| 0.08711 | 29.46 | 0.741 | 0.08590 | 34.80 | 0.725 | 0.08650 | 43.42 | 0.716 |
| 0.07946 | 29.63 | 0.736 | 0.07880 | 35.12 | 0.723 | 0.07900 | 43.80 | 0.713 |
| 0.07262 | 29.90 | 0.733 | 0.07190 | 35.46 | 0.720 | 0.07290 | 44.13 | 0.710 |
| 0.06621 | 30.21 | 0.731 | 0.06583 | 35.79 | 0.718 | 0.06623 | 44.60 | 0.708 |
| 0.06096 | 30.52 | 0.729 | 0.05993 | 36.19 | 0.716 | 0.06096 | 45.01 | 0.706 |
| 0.05581 | 30.87 | 0.728 | 0.05506 | 36.61 | 0.716 | 0.05506 | 45.56 | 0.704 |
| 0.05138 | 31.17 | 0.726 | 0.05040 | 36.95 | 0.714 | 0.05040 | 46.07 | 0.703 |
| 0.04719 | 31.45 | 0.724 | 0.04596 | 37.43 | 0.714 | 0.04656 | 46.50 | 0.702 |
| 0.04312 | 31.80 | 0.723 | 0.04229 | 37.78 | 0.712 | 0.04189 | 47.01 | 0.700 |
| 0.03988 | 32.12 | 0.722 | 0.03885 | 38.14 | 0.711 | 0.03926 | 47.33 | 0.698 |
| 0.03591 | 32.57 | 0.721 | 0.03582 | 38.46 | 0.709 | 0.03602 | 47.80 | 0.697 |
| 0.03326 | 32.87 | 0.720 | 0.03256 | 38.92 | 0.709 | 0.03278 | 48.29 | 0.696 |
| 0.03060 | 33.18 | 0.719 | 0.02992 | 39.28 | 0.707 | 0.02972 | 48.75 | 0.694 |
| 0.02812 | 33.45 | 0.717 | 0.02749 | 39.64 | 0.706 | 0.02709 | 49.24 | 0.692 |
| 0.02529 | 33.83 | 0.715 | 0.02505 | 40.01 | 0.705 | 0.02485 | 49.70 | 0.691 |
| 0.02307 | 34.16 | 0.714 | 0.02242 | 40.45 | 0.703 | 0.02285 | 50.11 | 0.690 |
| NaCMC in 70% EG–water | | | | | | | | |
| 0.10614 | 15.77 | 0.729 | 0.10304 | 19.66 | 0.715 | 0.10292 | 25.01 | 0.696 |
| 0.09728 | 15.87 | 0.724 | 0.09444 | 19.71 | 0.709 | 0.09452 | 25.00 | 0.688 |
| 0.08916 | 15.96 | 0.720 | 0.08656 | 19.85 | 0.706 | 0.08687 | 25.14 | 0.684 |
| 0.08171 | 16.09 | 0.716 | 0.07933 | 20.00 | 0.703 | 0.07962 | 25.28 | 0.681 |
| 0.07489 | 16.25 | 0.714 | 0.07271 | 20.14 | 0.700 | 0.07297 | 25.44 | 0.677 |
| 0.06864 | 16.41 | 0.712 | 0.06664 | 20.28 | 0.697 | 0.06688 | 25.62 | 0.674 |
| 0.06291 | 16.55 | 0.710 | 0.06107 | 20.42 | 0.694 | 0.06129 | 25.83 | 0.672 |
| 0.05766 | 16.71 | 0.708 | 0.05598 | 20.61 | 0.692 | 0.05618 | 26.03 | 0.669 |
| 0.05284 | 16.88 | 0.706 | 0.05130 | 20.78 | 0.690 | 0.05160 | 26.28 | 0.668 |
| 0.04843 | 17.04 | 0.704 | 0.04702 | 20.95 | 0.688 | 0.04719 | 26.53 | 0.667 |
| 0.04439 | 17.21 | 0.703 | 0.04309 | 21.15 | 0.687 | 0.04319 | 26.75 | 0.665 |
| 0.04068 | 17.38 | 0.702 | 0.03950 | 21.34 | 0.686 | 0.03964 | 26.99 | 0.664 |
| 0.03729 | 17.53 | 0.700 | 0.03620 | 21.53 | 0.684 | 0.03633 | 27.22 | 0.662 |
| 0.03413 | 17.70 | 0.698 | 0.03318 | 21.69 | 0.682 | 0.03330 | 27.48 | 0.661 |
| 0.03126 | 17.84 | 0.696 | 0.03041 | 21.91 | 0.682 | 0.03052 | 27.69 | 0.659 |
| 0.02860 | 18.00 | 0.695 | 0.02787 | 22.08 | 0.680 | 0.02797 | 27.92 | 0.658 |
| 0.02639 | 18.13 | 0.693 | 0.02554 | 22.27 | 0.679 | 0.02563 | 28.18 | 0.657 |
| 0.02417 | 18.29 | 0.691 | 0.02341 | 22.43 | 0.677 | 0.02349 | 28.43 | 0.656 |

Units: $\sqrt{c}$, $\mathrm{eqv}^{1/2}/\mathrm{L}^{1/2}$ and $\Lambda$, $\mathrm{S\,cm^2/eqv}$.

### 4.4. *Effect of temperature on counterion condensation*

The fraction of uncondensed counterions is found to decrease with increasing temperature over the entire polyelectrolyte concentration region in a given mixed solvent medium (*cf.* Table 3 and Fig. 2(b)). This can be ascribed to a change in the solvation and condensation behavior of counterions upon changing the temperature. Raising the temperature has the effect of (*a*) gradual desolvation for the counterions and the polyionic sites, and (*b*) reduction in medium relative permittivity; both effects promote polyion–counterion interactions and hence would result in an increased 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 (Sharma et al., 2009). A similar behavior was also observed for aqueous solutions of sodium and potassium dextran sulfates (Beyer & Nordmier, 1995) where an increase in the charge density parameter (and hence a decrease in the fraction of uncondensed counterions) was reported with the rise of temperature. Similar results were observed with NaCMC (Nandi & Das, 2005) and sodium polystyrenesulfonate (Ghosh et al., 2009) in mixed-solvent media earlier.

Moreover, decreasing effective charge on the polyion chain with increasing temperature causes less repulsion between the polyion charges and hence a coiling of the chain is expected as the temperature is elevated.

### 4.5. *Effect of medium on counterion condensation*

The measured fraction of uncondensed counterions is found to decrease with increasing EG content of the mixed solvent media at each temperature over the entire polyelectrolyte concentration range investigated (Table 3 and Fig. 2(a)). Since decreasing relative permittivity results in a greater interaction between the polyion and counterions (the degree of ionic solvation remaining the same over the entire EG–water composition range as has been established earlier (Das, 1994)), the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower – as has been observed in the present study. This has manifested an interesting influence on the polyion equivalent conductivity which is also found to decrease with decreasing relative permittivity of the mixed solvent media at each temperature

(Fig. 3(a)). This is clearly an indication of the decreasing effective charge on the polyion chain which results in a lower mobility of the polyion as the medium becomes richer in EG. Furthermore, decreasing effective charge on the polyion chain with increasing EG-content of the medium causes less repulsion between the polyion charges and hence a contraction of the chain is expected.

### 4.6. *The association constant ($K_A$) and the standard state free energies of counterion condensation ($\Delta G_A^0$) 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 condensation is essential. For this purpose, the values of the association constants (in liter per equivalents of the monovalently-charged groups) for the binding of the counterions onto to polyionic sites

$$\text{free site} + \text{Na}^+ \Leftrightarrow \text{combined site} \tag{8}$$

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

$$\ln K_\text{A} = \ln\left(\frac{1-f}{f}\right) - \ln(fc_\text{p}) \tag{9}$$

The standard state free energies of counterion condensation ($\Delta G_\text{A}^0$) can then be easily obtained from:

$$\Delta G_\text{A}^0 = -RT\ln K_\text{A} \tag{10}$$

where $R$ is the universal gas constant.

Fig. 4(a) displays the variation of $\Delta G_\text{A}^0$ values of NaCMC solutions as a function of the square root of the polyelectrolyte concentration in six different EG–water mixtures containing 0, 10, 20, 30, 50 and 70 mass% of EG at 35 °C over the entire concentration range investigated. Fig. 4(b), on the hand, shows the polyelectrolyte concentration dependence of the $\Delta G_\text{A}^0$ values at a representative mass percent of EG (namely 30 mass%) in three different temperatures mentioned. The negative $\Delta G_\text{A}^0$ 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 EG to the medium makes the counterion condensation process more favorable as expected. The spontaneity of the counterion condensation process is, also, found to increase as the temperature increases in a given mixed solvent.

### 4.7. *Transference number ($T_p$) of the carboxymethylcellulose anion in EG–water mixed solvent media and its variation with polyelectrolyte concentration, solvent medium and temperature*

The transference number of the polyion ($T_\text{p}$) has been obtained from the equivalent conductivity of the polyion obtained earlier ($\lambda_\text{p}$) and the experimentally determined equivalent conductivity of the polyelectrolyte as a whole ($\Lambda$) using the following relationship

$$T_\text{p} = \frac{\lambda_\text{p}}{\Lambda} \tag{11}$$

In Fig. 5(a) we present the transference number data of the polyion as a function of the square root of the polyelectrolyte concentration in various EG–water mixed solvent media at 30 °C. Fig. 5(b), on the other hand, shows the influence of temperature on the $T_\text{p}$ *vs.* $\sqrt{c}$ profiles in a given EG–water mixed solvent medium (30 mass% EG). The polyion transport number values are always found to be greater than 0.5 but less than unity over the entire concentration range investigated in this work, and decrease monotonically with increasing polyelectrolyte concentration. It is apparent that the major proportion of the current is carried by the polyions in the investigated systems. The present observation that the transference number of the polyion is always larger than 0.5 fits into comparable literature reports on aqueous solutions of polystyrenesulfonic acid and its salts (Džudževič, Vlachy, & Bratko, 1991; Špan, Bratko, Dolar, & Feguš, 1983) and on aqueous solutions of poly(anetholesulfonic acid) (Lipar-Oštir, Zalar, Bešter-Rogač, Pohar, & Vlachy, 2009) where the polyion transference numbers are found to be greater than 0.5 and in some cases these are even found to be greater than unity. When the polyion transference number is greater than unity, that of the counterion would, consequently, be negative; this points out to the fact that a fraction of the counterions is associated with the polyions and travels with them toward (in the case of polyanions) the positive electrode.

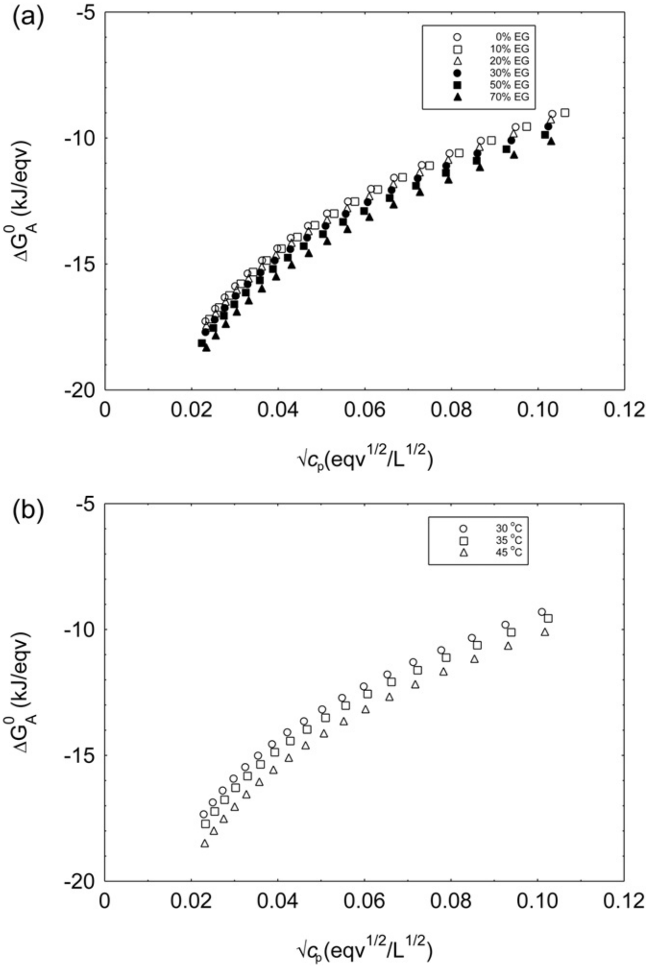

**Fig. 4.** (a) Concentration dependence of the standard state free energy change ($\Delta G_\text{A}^0$) in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% EG) at 35 °C. (b) Concentration dependence of the standard state free energy change ($\Delta G_\text{A}^0$) in EG–water mixed solvent medium containing 30 mass% of EG at 30, 35, and 45 °C.

### 4.8. *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)

$$f_\text{ps} = \frac{|z_\text{p}|fF^2}{\lambda_\text{p}} \tag{12}$$

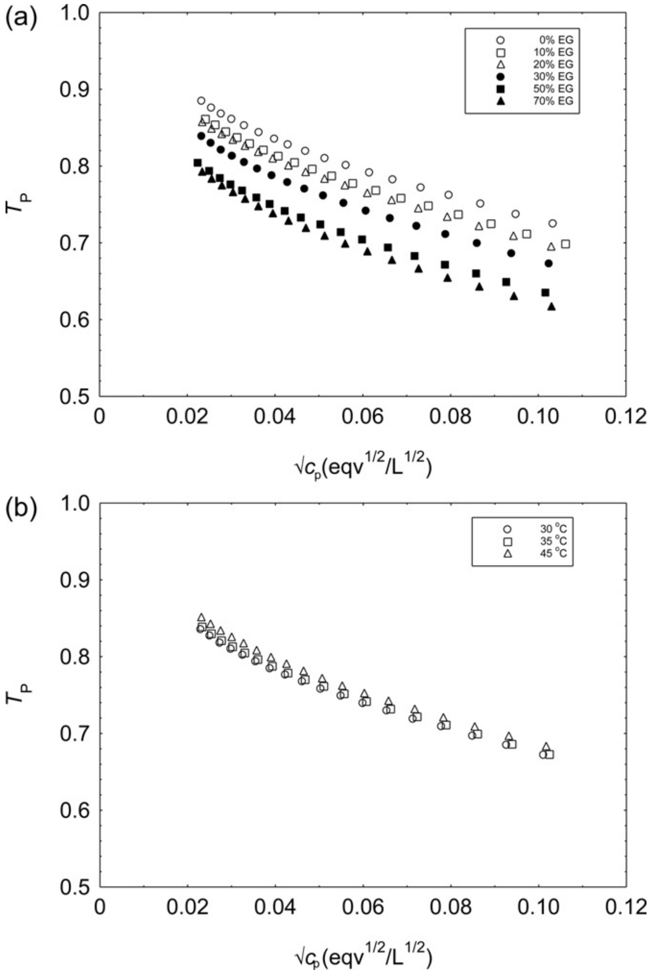

**Fig. 5.** (a) Concentration dependence of the transference number ($T_p$) in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% of EG) at 35 °C. (b) Concentration dependence of the transference number ($T_p$) of the carboxymethylcellulose ion in EG–water mixed solvent medium containing 30 mass% of EG at 30, 35, and 45 °C.

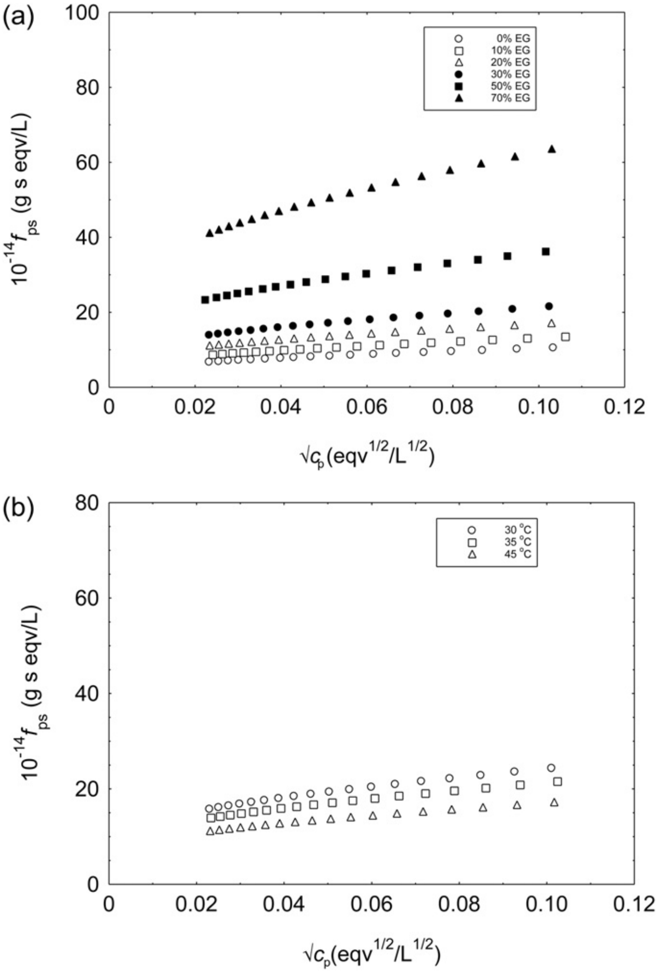

**Fig. 6.** (a) Concentration dependence of the coefficient of friction between carboxymethylcellulose ion and the solvent ($f_{ps}$) in different EG–water mixtures (containing 0, 10, 20, 30, 50, and 70 mass% of EG) at 35 °C. (b). Concentration dependence of the coefficient of friction between carboxymethylcellulose ion and the solvent ($f_{ps}$) in EG–water mixed solvent medium containing 30 mass% of EG at 30, 35, and 45 °C.

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. 6(a) and (b). Fig. 6(a) shows the dependence of $f_{ps}$ on $\sqrt{c_p}$ in 0, 10, 20, 30, 50 and 70 mass% EG–water mixtures each at 30, 35, and 45 °C respectively. Influence of temperature on the concentration dependence of the $f_{ps}$ values at a given mass percent of EG (30 mass%) is depicted in the representative Fig. 6(b).

It is evident from Fig. 6(a) that the friction coefficients of the monomer units increase with increasing EG content of the mixture over the entire polyelectrolyte concentration range at a given temperature. Fig. 6(b), on the other hand, reveals a decrease in the monomer friction coefficients as the temperature is elevated in any given mixed solvent medium.

Now, the friction between a monomer unit of the polyion and the solvent medium varies directly with three factors: (*i*) the coefficient of viscosity of the medium, (*ii*) the size of the polyion as a whole, and (*iii*) the mobility of the polyion, and in what follows we will discuss the relative contributions of these factors with respect to the solvent composition and the temperature toward the overall friction coefficient.

For the present system, at each temperature with increasing amount of EG in the mixed solvent media, the first factor increases (Table 1) whereas the second and the third decrease (see above). Fig. 6(a), manifesting an increase in the friction coefficients of the monomer units with the EG-content of the media, thus, indicates clearly that the influence of the viscosity of the medium becomes more important than the combined influences of the second and the third factors as the medium becomes richer in EG.

Effect of temperature on the friction coefficients of monomers in a given EG–water system (*cf*. Fig. 6(b)), on the other hand, reveal that the second factor joins force with the first in controlling the frictional behavior of the polyion with respect to temperature. A decrease in the friction coefficients with temperature demonstrates that the resultant contribution of the decreases in the viscosity of the medium and in the polyion size overrides the contribution of the increase in the polyion mobility to the friction coefficient upon temperature elevation.

## 5. Conclusions

An investigation on the electrical conductivity of salt-free solution of an anionic polyelectrolyte – sodium carboxymethylcellulose – in ethylene glycol–water mixed solvent media has been performed as a function of polymer concentration at three different temperatures. 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 results have been analyzed in terms of a recent model based on the scaling approach for the configuration of a polyelectrolyte chain in semidilute solution has, to determine the fractions of uncondensed counterions. The results suggest that the effective charge on the polyion chain, incorporating any effect of counterion condensations, depends on the polymer concentration. 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, (*iv*) the polyion transference numbers, and (*v*) 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.

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## References

Abramovic, H., & Klofutar, C. (1997). Conductivity of some tetra-n-alkylammonium salts of pectic acid. *European Polymer Journal*, *33*, 1295–1300.

Barraza, R. G., & Rios, H. E. (1995). Counterion association to cationic polyelectrolyte 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.

Bhattarai, 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., & Das, C. (2011). Polyion-counterion interaction behavior for sodium carboxymethylcellulose in methanol-water mixed solvent media. *Carbohydrate Polymers*, *87*, 1144–1152.

Cleland, R. L. (1991). Electrophoretic mobility of wormlike chains. 2. Theory. *Macromolecules*, *24*, 4391–4402.

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. (1994). A study on the preferential solvation of ions in mixed aqueous binary solvent systems using the scaled particle theory. *Bulletin of the Chemical Society of Japan*, *67*, 1217–1220.

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., Jager, 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.

Džudževič, H., Vlachy, V., & Bratko, D. (1991). Effect of temperature on electrical transport and ion binding in poly(styrenesulfonate) solutions. *European Polymer Journal*, *27*, 1195–1200.

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.

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.

Kwak, J. C., Murphy, G. F., & Spiro, E. J. (1978). The equivalent conductivity of aqueous solutions of alkali metal salts of a number of ionic polysaccharides. *Biophysical Chemistry*, *7*, 379–386.

Lipar-Oštir, I., Zalar, P., Bešter-Rogač, M., Pohar, C., & Vlachy, V. (2009). Electric conductivity of aqueous solutions of poly(anetholesulfonic acid) and its alkaline salts. *Journal of Physical Chemistry B*, *113*, 2705–3211.

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.

Manning, G. S. (1981). Limiting laws and counterion condensation in polyelectrolyte solutions: Electrophoretic mobility and conductance. *Journal of Physical Chemistry*, *85*, 1506–1515.

Manning, G. S. (1996). The critical onset of counterion condensation: A survey of its experimental and theoretical basis. *Berichte der Bunsengesellschaft für Physikalische Chemie*, *100*, 909–922.

Mohanty, U., & Zhao, Y. (1996). Polarization of counterions in polyelectrolytes. *Biopolymers*, *38*, 377–388.

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. In *ACS symposium series 548*. Washington, DC: American Chemical Society.

Sharma, R., Das, C., Chatterjee, A., & Das, B. (2009). Electrical conductances of tetrabutylammonium bromide, sodium tetraphenylborate, and sodium bromide in ethylene glycol (1) + water (2) mixtures at (298.15, 303.15, 308.15, and 318.15) K. *Journal of Chemical and Engineering Data*, *54*, 1899–1904.

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.

Špan, J., Bratko, D., Dolar, D., & Feguš, M. (1983). Electrical transport in polystyrenesulfonate solutions. *Polymer Bulletin*, *9*, 33–39.

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 polygalactouronate. *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.