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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 ε. 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_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, 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 ξ_e. This means that for length scales less than ξ_0, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0.

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

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

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 λ_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 (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 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 λ_c^0 values of sodium ion.

t (°C)	Mass % of EG	Coefficient of viscosity (mPa s)	Relative permittivity	λ_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