Thermodynamic, transport and frictional properties in semidilute aqueous sodium carboxymethylcellulose solution

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ABSTRACT

Electrical conductivities of aqueous solutions of an anionic polyelectrolyte sodium carboxymethylcellulose with different degrees of substitution have been reported as a function of concentration and temperature. The conductance-concentration data have been analyzed with the modified Manning counterion-condensation model appropriate for semidilute polyelectrolyte solutions, considering the de Gennes scaling description of the polyion configuration. 36–55% of the counterions were found to remain condensed and the condensation process was shown to be spontaneous. Although the level of counterion-condensation depends appreciably on the degree of substitution, it was found to remain invariant with the polyelectrolyte concentration and the temperature. The free energies of counterion-condensation, the ratios of the mobility of the polyion to that of the counterion, the polyion transference numbers, and the coefficients of monomer-solvent friction have been evaluated. The effects of the polyion charge, its size, and the bulk viscosity of the media on the polyion-counterion interactions have also been discussed.

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1. Introduction

Polymers with repeat units bearing an electrolyte group are referred to as polyelectrolytes. These groups dissociate in polar solvent media, conferring charges to the polymers to yield a multivalent polyion and a large number of counterions of opposite charge. The strong electric field causes a distinct correlation of the counterions with the polyion thus leading to what is commonly known as the "condensation" of a certain fraction of the counterions onto the polyion. The concept of counterion condensation, which is central to the solution behavior of polyelectrolytes, was originally introduced by Oosawa's two-phase model [1,2]. This idea was later fully exploited by Manning who derived the well-known limiting laws for salt-free solutions of linear polyelectrolytes [3–6]. In particular, Manning derived limiting laws for a number of thermodynamic and transport properties of polyelectrolytes in solution e.g., osmotic coefficient, electrophoretic mobility, equivalent conductance etc. It must, however, be kept in mind that these laws apply only to infinitely dilute solutions which cannot be attained experimentally.

The Manning model has been recently successfully extended by Colby and co-worker [7,8] to describe the dielectric and conductometric behavior of flexible polyelectrolyte systems having finite concentrations on the basis of the scaling picture for the chain conformation of a polyelectrolyte in solution. The predictions for the conductivity of semidilute polyelectrolyte solutions have been compared with the experimental data and found to provide satisfactory descriptions [7,13].

A survey of the literature indicated that the influences of polyelectrolyte concentration, polyelectrolyte molecular weight, medium, and temperature on counterion condensation in salt-free polyelectrolyte solution have been fairly investigated [7–18].

Another important parameter, namely the degree of substitution of the polyelectrolyte sample defined as the average number of dissociable groups per monomer unit in a polyion, should have a profound influence on the counterion condensation behavior. This can be conceived if one considers the charge density parameter of a polyelectrolyte defined through the ratio of the Bjerrum length (λ_B) to the contour distance per unit charge (b):

$$\xi = \frac{\lambda_B}{b}. \tag{1}$$

The Bjerrum length $\lambda_B = e^2/\varepsilon k_B T$ is the length scale where the Coulomb interaction energy between two elementary charges and the thermal energy are equal (e is the elementary charge, ε the relative permittivity of the solvent medium, k_B the Boltzmann constant and T the temperature in absolute scale). With the

variation of the degree of substitution, the value of b will vary which, in turn, will result in a changed charge density parameter value. The extent of counterion condensation onto the polyion chain should also be affected. This aspect, however, has not been fully explored, in particular, with respect to its temperature dependence till date despite its importance in the elucidation of the interactions prevailing in polyelectrolyte solutions. This prompted us to undertake a comprehensive program to investigate the counterion-condensation phenomena in aqueous solution of sodium carboxymethylcellulose with varying degrees of substitution. Furthermore, the influences of polyelectrolyte concentration, and temperature will also be taken into consideration. Electric conductivity has been employed as a convenient probe to quantify the fractions of free counterions as it measures the contribution of every charged entity present in a solution under the influence of an external electric field.

The polyelectrolyte chosen in this study is an important industrial polymer with a wide range of applications in detergents, textiles, paper, food, drugs, and oil well drilling operations [19,20]. As shown in Fig. 1, carboxymethylcellulose is a derivative of cellulose with carboxymethyl groups (–CH$_2$COOH) substituting some of the hydroxyl groups (–OH) of cellulose. The degree of substitution indicates the average number of carboxymethyl groups in a monomer unit, which significantly affects the properties of carboxymethylcellulose. The degree of substitution can vary from 0 to 3. The hydrogen ions in the carboxymethyl groups are generally substituted by the alkali ions used as catalysts during the synthesis of carboxymethylcellulose from cellulose. Sodium ions are commercially used and thus sodium carboxymethylcellulose is a cellulose material containing sodium-substituted carboxymethyl groups (–CH$_2$COONa).

This article has been organized as follows. In the next section, a brief description of the modern theory of electrical conductivity of semidilute polyelectrolyte solution is appended, and a summary of the main prediction of the scaling theories of polyelectrolyte solution according to the model proposed by Rubinstein and coworkers [21–24]. The Experimental section provides a hint to the chemical characterization of the polyelectrolyte samples studied along with an account of the experimental techniques employed. In the Results and Discussion section, the counterion-condensation behavior of the investigated sodium carboxymethylcellulose solutions in aqueous media has been assessed with particular reference to its dependence on the degree of substitution of the polyelectrolyte sample, its concentration, and the experimental temperature. We also considered the thermodynamics of counterion-condensation, frictional behavior of the monomer units and the transference behavior of the polyion and counterion in this section. Finally, the Conclusions section summarizes the important conclusions derived from the present study.

2. Scaling theory of electric conductivity of semidilute polyelectrolyte solution

Scaling concepts, successfully used for uncharged polymers, have been applied to the description of the chain conformation
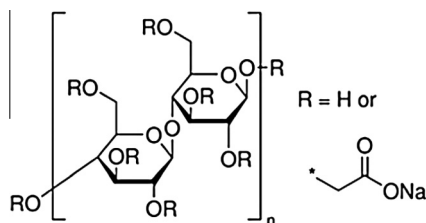

Fig. 1. Chemical structure of sodium carboxymethylcellulose.

of polyelectrolyte solutions in different concentration regimes by de Gennes et al. [25,26], Odijk [27], Grosberg and Khokhlov [28] and more recently by Rubinstein and co-workers [21–24].

In a semidilute solution of polyelectrolytes, a polyion chain has been considered as an assembly of randomly walking N_ξ correlation blobs each with a size of ξ_0. Each correlation blob consists of g monomers and carries an electric charge of $q_\xi = |z_c|efg$, z_c being the charge on the counterion. The whole chain which has a contour length of $N_\xi\xi_0$, bears a charge of $|z_c|efgN_\xi$. The strong electrostatic interactions within the correlation blobs cause the chain to attain a completely extended conformation of g_e electrostatic blobs each of size D.

Based on this model, Colby et al. [7,8], derived the following expression of the equivalent conductivity of a salt-free solution of a polyion (λ_p)

$$\lambda_p = \frac{F|z_c|efg\ln(\xi_0/D)}{3\pi\eta\xi_0}, \tag{2}$$

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

The equivalent conductivity (Λ) of the polyelectrolyte solution was given by

$$\Lambda = f\left[\lambda_c^0 + \frac{F|z_c|efg\ln(\xi_0/D)}{3\pi\eta\xi_0}\right]. \tag{3}$$

λ_c^0 being the limiting equivalent conductivity of the counterions.

The size of the electrostatic blob (D) and that of the correlation blob (ξ_0) appearing in Eq. (3) are governed by the quality of the solvent. For poor solvents, these are given by [7]

$$D \cong b\left(\frac{b}{f^2\lambda_B}\right)^{1/3}, \tag{4}$$

$$\xi_0 \cong (cb)^{-1/2}\left(\frac{b}{f^2\lambda_B}\right)^{1/3}, \tag{5}$$

where c is the number density of monovalent charged groups.

For good solvents, on the other hand, the values of D and ξ_0 are given by [27]

$$D \cong b\left(\frac{b}{f^2\lambda_B}\right)^{3/7}, \tag{6}$$

$$\xi_0 \cong (cb)^{-1/2}\left(\frac{b}{f^2\lambda_B}\right)^{1/7}. \tag{7}$$

Now, since the specific conductivity (σ) of the polyelectrolyte solution is related to the equivalent conductivity through $\sigma = \Lambda c/N_A$ (N_A being the Avogadro number), it is given by

$$\sigma = \frac{fc}{N_A}\left[\lambda_c^0 + \frac{F|z_c|efg\ln(\xi_0/D)}{3\pi\eta\xi_0}\right]. \tag{8}$$

As can be seen, the above equation has a single free parameter, the fraction f of free counterions that defines the fraction of the effectively ionized group along the polyion chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to a polyelectrolyte solution which is infinitely dilute, Eq. (8) can be applied to more concentrated systems.

3. Experimental

Sodium carboxymethylcellulose with a molecular weight of 250,000 was purchased from Aldrich Chemical Company, Inc. Three polyelectrolyte samples with degrees of substitution of 0.7