The Effects of Concentration, Relative Permittivity and Temperature on the Transport Properties of Sodium Polystyrenesulphonate in Methanol–Water Mixed Solvent Media

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Abstract

Precise measurements on the electrical conductivity of solutions of sodium polystyrenesulphonate in methanol–water mixed solvent media containing 8, 16, 25, and 34 wt.% of methanol at 308.15, 313.15, 318.15, and 323.15 K are reported. The degree of substitution of sodium polystyrenesulphonate used was 1, and the concentrations were varied from $\sim 2.0 \times 10^{-4}$ to $\sim 4.0 \times 10^{-3}$ monomol $l^{-1}$. The results showed a slight and monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration. The applicability of the Manning’s theory for salt-free polyelectrolyte solution was examined and a major discrepancy against the theory was observed. The calculated values of the equivalent conductivity deduced on the basis of this theory were found to be lower than the experimental ones. Possible reasons for this discrepancy have been discussed. The effects of the temperature and relative permittivity of the medium on the equivalent conductivity were also investigated. Estimation of the fractions of uncondensed counterions provides important insight regarding the solution behavior of the polyelectrolyte in methanol–water mixtures.

Introduction

Polyelectrolytes are polymers having ionizable groups, which in polar solvents, can dissociate into charged polymer chains (macroion) and small counterions of opposite charge [1, 2]. Solution properties of polyelectrolytes, both in the presence and in the absence of added salt, differ considerably from those of neutral macromolecular solutions or those of simple electrolytes. The origin of this specificity lies in the combination of properties derived from long-chain molecules with those derived from charge interactions. The high charge density on the macroion produces a strong ionic field which attracts counterions. This strong ionic interaction is the source of the characteristic properties of polyelectrolytes. Current interest in charged polymer solutions, in particular in high-molecular weight ionic macromolecules, is supported by the needs of biophysics since biopolymers are usually charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behavior [3]. In accounting for the solution behavior of biological and synthetic polyelectrolytes, elucidation of the interactions between counterions and charged groups on the polyeion are of essential importance. Polyelectrolyte effect includes both deviations from the behavior of neutral polymers caused by the existence of charges along the polymer chain and deviations from the behavior of the electrolytes caused by the fixation of one sort of charges on the polymer chain. Therefore, in addition to the method of macromolecular characterization, electrochemical techniques have also been applied to investigate the solution behavior of polyelectrolytes. The specific conductance and the equivalent conductivity, $\Lambda$, are experimentally determined parameters which are suitable to describe the electrolytic transport properties of polyelectrolyte solutions because these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field. In spite of various attempts by different investigators, a completely satisfactory theory to describe the electrolytic conductivity of polyelectrolyte solutions has not yet been developed [4–6].

However, the description of different electrical properties of polyeions in aqueous solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory [7–10] that, under some aspects, can be considered equivalent to the Poisson–Boltzmann cylindrical cell model [11–15]. Within this model, the polyeion is represented as an infinitely long charged line, small ions (counterions) are assumed to form an ionic atmosphere whose density depends on the frame
of the polion and their interactions with the charged polion groups are purely Coulombic, so that the screening effect extends over the Debye–Hückel length. The uncondensed mobile ions are treated in the Debye–Hückel–Hückel approximation. The solvent is assumed to be a continuous medium characterized by a spatially uniform dielectric constant. Interactions among polions are neglected, the theory being addressed to highly diluted solutions. The basic idea is that if the charge density (ζ) of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy k_BT. On the basis of these assumptions, this approach has been successfully applied to different polyelectrolyte systems, and numerous experiments have strongly suggested the validity of this model [16–22].

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by [7, 23, 24]

\[ \xi = \frac{e^2}{bDk_BT} \]

(1)

where \( e \) is the protonic charge, \( D \) the relative permittivity of the medium, \( b \) the spacing between charged groups taken along the axis of the polion chain, \( k_B \) the Boltzmann constant and \( T \) the temperature in absolute scale. This theory states that if \( \xi > 1 \), enough counterions condense onto the polion to yield the critical value \( \xi = 1 \). If, on the other hand, \( \xi < 1 \), ionization takes place to reach this critical value. A limiting law of electrical conductivity for a salt-free polyelectrolyte solution is related to \( \xi \) by the following equation [8, 23, 25]

\[ \Lambda = f (\lambda_c^0 + \lambda_p) \]

(2)

where \( \lambda_c^0 \) and \( \lambda_p \) are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polion at a finite concentration, respectively, and \( f \) is counterion–polion interaction parameter given by [7, 23, 24]

\[ f = \frac{0.866}{\xi} \]

(3)

In contrast to Huizenga, [26] where the counterions are regarded either as “bound” or as “free” implying that they are not influenced by the polion, Manning assumed that while the condensed counterions, certainly qualify as bound, the fraction of such ions is \( 1 - \xi^{-1} \neq 1 - f \), the uncondensed counterions may, in no way, be thought of as free, being subjected to the Debye–Hückel potential of the polions. Thus \( f \) does not have the significance of free counterions rather it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, \( \lambda_p \) has been derived theoretically for the cylinder model of polyelectrolyte [9], and it follows for counterions with a charge of \( z_c \)

\[ \lambda_p = \frac{2794|z_c|^{-1}ln(\kappa a)}{1 + 43.2A |z_c|_0^{-1}ln(\kappa a)} \]

(4)

where the parameter \( a \) is the radius of the polymer chain, while

\[ A = \frac{Dk_BT}{3\pi\eta_0 e} \]

(5)

with \( \eta_0 \) being the coefficient of viscosity of the solvent. In Equation (5), \( \kappa \) is the Debye screening constant, which is defined by

\[ \kappa^2 = \frac{4\pi e^2}{Dk_BT} \xi^{-1} n_c |z_c| \]

(6)

where \( n_c \) is the stoichiometric equivalent polion concentration (monovalent charged groups per unit volume).

As far as we know there is very little work in the literature dealing with the effect of the medium and temperature on the interaction between a polion and its counterions [1, 27–29]. In this paper, the results are reported for conductivity measurements on sodium polystyrene-sulphonate, an anionic polyelectrolyte, in methanol–water mixed solvent media with varying relative permittivity at different temperatures. The aim of the present work is to

<table>
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<th>Temperature (K)</th>
<th>( \rho_0 ) (g cm(^{-3}))</th>
<th>( \eta_0 ) (mPa s)</th>
<th>( D )</th>
<th>( \lambda_c^0 ) (S cm(^2) mol(^{-1}))</th>
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