

Effects of Concentration, Relative Permittivity, and Temperature on the Solution Behavior of Sodium Carboxymethylcellulose As Probed by Electrical Conductivity

Prabir Nandi and Bijan Das*

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

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Precise measurements on the electrical conductivity of solutions of sodium salt of carboxymethylcellulose in acetonitrile/water mixed-solvent media containing 10, 20, and 40 vol % of acetonitrile are reported as a function of temperature. The degree of substitution of carboxymethylcellulose used was 0.70, and the concentrations were varied from $\sim 1 \times 10^{-4}$ to $\sim 1 \times 10^{-2}$ equiv L⁻¹. The results showed a decrease in the equivalent conductivity with increasing polyelectrolyte concentration. The applicability of Manning's theory for salt-free polyelectrolyte solutions 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 higher than the experimental ones. Possible reasons for this discrepancy have been discussed. The fractions of uncondensed counterions were evaluated, and these were found to depend on the polyelectrolyte concentration. The effects of the temperature and relative permittivity of the medium on the equivalent conductivity as well as on the fraction of uncondensed counterions were also investigated.

1. Introduction

In accounting for the solution behavior of biological and synthetic polyelectrolytes, interactions between counterions and charged groups on the polyion are of essential importance. The polyelectrolyte effect includes both deviation from the behavior of neutral polymers caused by the existence of charges along the polymer chain and deviation from the behavior of the electrolytes caused by the fixation of one sort of charge 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, Λ , are experimentally determined parameters that 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.^{1–3} However, recent interpretation of the polyelectrolyte conductivity has relied primarily on the Manning model^{4–8} for dilute solutions.

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge-density parameter defined by^{4,6,9}

$$\xi = \frac{e^2}{bDk_B T} \quad (1)$$

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 polyion 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 polyion 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 ξ by the following equation:^{5,6,10}

$$\Lambda = f\lambda_c^0 + \lambda_p \quad (2)$$

In eq 2, λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is the counterion–polyion interaction parameter given by^{4,6,9}

$$f = \frac{0.866}{\xi} \quad (3)$$

In contrast to Huizenga et al.,¹¹ where the counterions are regarded either as “bound” or as “free”, implying that they are not influenced by the polyion, Manning assumed that the unbound counterions are influenced by the Debye–Huckel potential of the polyions. Thus, f does not have the significance of the fraction of free counterions; rather, it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolytes,⁷ and it follows for counterions with 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 polymer chain, while

$$A = \frac{Dk_B T}{3\pi\eta_0 e} \quad (5)$$

with η_0 being the coefficient of viscosity of the solvent. In eq

* Corresponding author. E-mail: bijan_dasus@yahoo.com.

TABLE 1: Properties of Acetonitrile/Water Mixtures Containing 10, 20, and 40 Vol % of Acetonitrile at 308.15, 313.15, and 318.15 K and the Corresponding λ_c^0 Values

T/K	$\eta_0/\text{mPa s}$	D	$\lambda_c^0/\text{S cm}^2 \text{ mol}^{-1}$
10% Acetonitrile			
308.15	0.8766	72.15	58.81
313.15	0.7622	69.89	65.15
318.15	0.6773	68.27	70.50
20% Acetonitrile			
308.15	0.9067	67.94	56.21
313.15	0.7833	66.38	62.77
318.15	0.6984	64.84	68.03
40% Acetonitrile			
308.15	0.8200	60.07	51.50
313.15	0.6803	58.87	57.84
318.15	0.5611	57.32	65.34

5, κ is the Debye screening constant, which is defined by

$$\kappa^2 = \frac{4\pi e^2}{Dk_B T} \epsilon^{-1} n_c |z_c| \quad (6)$$

where n_c is the stoichiometric equivalent polyion 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 polyion and its counterions.^{12–14} In this paper, the results are reported for conductivity measurements on the sodium salt of carboxymethylcellulose (NaCMC), a substituted polysugar with limited flexibility, in acetonitrile/water mixed-solvent media with varying relative permittivity at different temperatures. The aim of the present work is to analyze the influence of the concentration, medium, and temperature on the extent of polyion–counterion interaction and on the mobility of the polyelectrolyte species. The experimentally determined equivalent conductivity values will also be compared with those obtained theoretically from the Manning counterion condensation theory.

2. Experimental Section

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.76570 \text{ g cm}^{-3}$ and a coefficient of viscosity of 0.3126 mPa s at 308.15 K ; these values are in good agreement with the literature values.¹⁵ Triply distilled water with a specific conductance of less than $10^{-6} \text{ S cm}^{-1}$ was used for the preparation of the mixed solvents. The physical properties of the acetonitrile/water mixed solvents used in this study at the experimental temperatures are reported in Table 1. The relative permittivities of the acetonitrile/water mixtures at the experimental temperatures were obtained with the equations as described in the literature,¹⁶ using the literature density and relative permittivity data of the pure solvents^{15,17} and the densities of the mixed solvents given in Table 1. Literature data on experimental relative permittivity values at temperatures and solvent properties relevant to the present study are unavailable with the exception of those at 308.15 K .¹⁸ Even at that temperature, the relative permittivities were not reported at the composition in which the conductance measurements have been carried out. Therefore, a direct comparison is not possible. However, the available literature values were plotted against the volume percent of methanol, and the permittivity values were generated from the smooth master plot; these values are found to be in good agreement with our values.

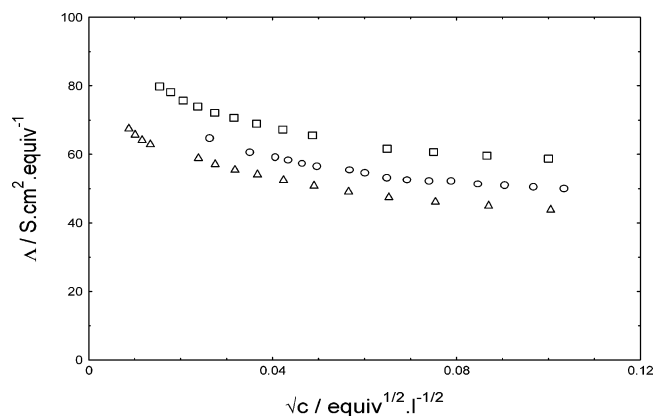


Figure 1. Equivalent conductivities (Λ) of NaCMC as a function of the square root of the polymer concentration (\sqrt{c}) at a temperature of 308.15 K in different acetonitrile/water mixtures: squares, 10% acetonitrile; circles, 20% acetonitrile; triangles, 40% acetonitrile.

NaCMC employed in these investigations was purchased from Aldrich Chemical Co., Inc. The average molecular weight of the sample was ca. 90 000 with a degree of substitution of 0.70, and these values agree well with those obtained from physico-chemical characterization in the present study.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz , using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01% . The cell was calibrated by the method of Lind and co-workers,¹⁹ using an aqueous potassium chloride solution. The measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.^{19,20} Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

To avoid moisture pickup, all of the solutions were prepared in a dehumidified room with the utmost care. In all cases, the experiments were performed in at least three replicates.

3. Result and Discussion

3.1. Experimental Equivalent Conductivity. Figures 1–3 show the variation of experimental equivalent conductivity of the investigated solutions of the NaCMC as a function of the square root of the concentration at different temperatures. From these figures, it is evident that the present species demonstrates typical polyelectrolyte behavior, in which the equivalent conductivities exhibit a slight increase in conductivity with decreasing concentration, bending up at low concentrations.

The effects of temperature and relative permittivity on the equivalent conductivity values are directly evident from these figures. At each temperature, the Λ values are found to decrease with decreasing relative permittivity in going from 10 to 40% acetonitrile/water mixtures over the entire concentration range investigated. This is expected because, as the relative permittivity of the medium decreases, interaction between a polyion and counterions increases, which results in a lower mobility of the conducting species and, hence, the polyelectrolyte as a whole. Increasing temperature, on the other hand, is expected to increase the mobility, as manifested in these figures.

3.2. Comparison with the Manning Counterion Condensation Theory. Now we will compare the experimental values

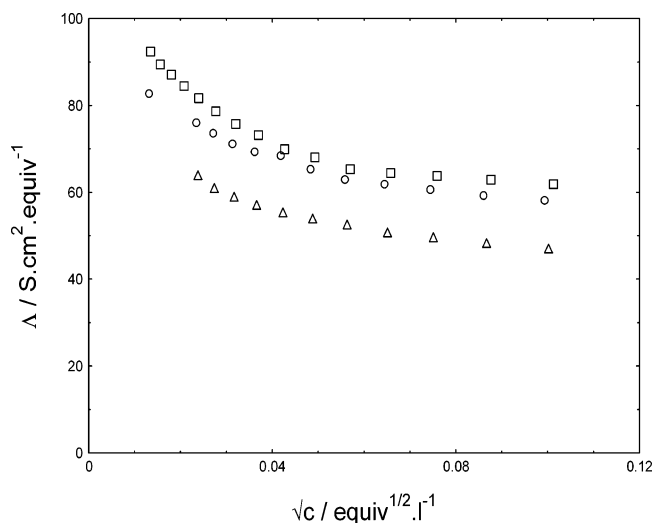


Figure 2. Equivalent conductivities (Λ) of NaCMC as a function of the square root of the polymer concentration (\sqrt{c}) at a temperature of 313.15 K in different acetonitrile/water mixtures: squares, 10% acetonitrile; circles, 20% acetonitrile; triangles, 40% acetonitrile.

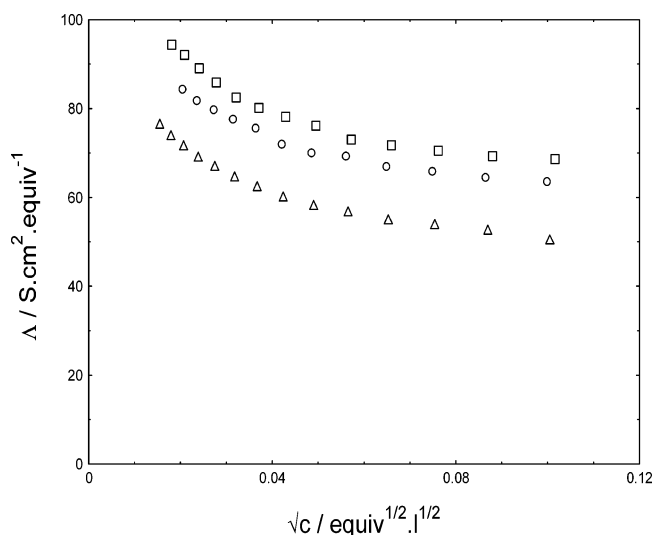


Figure 3. Equivalent conductivities (Λ) of NaCMC as a function of the square root of the polymer concentration (\sqrt{c}) at a temperature of 318.15 K in different acetonitrile/water mixtures: squares, 10% acetonitrile; circles, 20% acetonitrile; triangles, 40% acetonitrile.

of equivalent conductivity with those calculated using the Manning counterion condensation theory (eqs 2–4).

In obtaining the theoretical equivalent conductivities, the required values for the limiting equivalent conductivity of the counterion, λ_c^0 , in 20 and 40 vol % of acetonitrile mixtures were taken from the literature,²² while those in a 10 vol % mixture were determined in the present work by measuring the electrical conductivities of sodium bromide, sodium tetraphenylborate, and tetrabutylammonium bromide following the procedure described earlier,²⁰ and these are given in Table 1. The charge-density parameters, ξ , were calculated using a segment length²¹ of 5.15 Å, considering a degree of substitution of 0.70, and these are included in Table 2. The theoretical values of λ_p and, hence, Λ are dependent on a , the radius of the polyion cylinder. Obviously, the assignment of a cylindrical radius to any polymer chain can only be a rough approximation at best, but fortunately λ_p is not strongly dependent on a and the change in concentration dependence of λ_p upon varying a between realistic values is small. A cylindrical radius of 7 Å was used for the present analysis.²²

A graphical representation of the experimental values (points) along with the theoretical predictions (solid lines) is given in Figure 4 at a selected temperature in acetonitrile/water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably lower than the theoretical values calculated using the charge-density parameter, ξ , following from the molecular structure of the polyelectrolyte, and the concentration dependence of Λ also deviates from the theoretically predicted dependence (cf. Figure 4). The same situation of positive deviation,^{23,24} as well as negative deviation,^{25,26} from the experimental values was also noticed for other polyelectrolytes in aqueous solutions. The present data show a stronger increase in Λ with dilution at very low concentrations than the predicted values. The discrepancy between experimental and predicted Λ values for NaCMC in all acetonitrile/water mixtures and at all temperatures investigated is very similar. Higher calculated equivalent conductivities are, therefore, a consequence of the Manning theory, which predicts too-large values for the fraction of uncondensed counterions.

It is interesting to note that the equivalent conductivity calculated here is found to be highly sensitive toward ξ , and a semiquantitative description of the experimental data is obtained only if the charge-density parameter ξ is raised from its structural value. The short-dashed lines in Figure 4 display the respective calculation using the optimum values of ξ , which provide fairly satisfactory fits. The charge-density parameters, ξ , which describe the experimental results best, along with the respective standard deviation of fits are given in Table 2. In the case of this partially flexible polyelectrolyte, this could be rationalized by assuming an “effective charge-density parameter” that is higher than the value obtained from the structural data and adjusted to match the experimental data.¹ The reason for a higher effective ξ was sought in the locally curved conformation of the flexible polyion chain. The counterions then “see” an effective chain being more highly charged than the fully stretched chain. Hence, their mobility is lowered concomitantly. Other possible reasons for the observed differences between the experimental and theoretical values include deviation from the rodlike model because of possible kinking in the structure of the polyelectrolyte, the presence of neutral sugar inclusion in the polyion chain, possible polyion–polyion interaction, interaction between the uncondensed counterions, and specific interaction between a polyion and the counterions.^{9,27–30} Another possible reason may be sought in a locally varying relative permittivity. The immediate neighborhood of the macroion may exhibit a considerably lower relative permittivity than the bulk.³¹ This must necessarily lead to a stronger interaction of the macroion with the counterions, as observed in the present investigation. A further possibility is that the Manning theory, based on the assumption of an infinitely long polymer chain model, might be inadequate for treating condensation phenomena, because in the limit of dilution it was found that counterion condensation does not occur for a polyion of finite length.

3.3. Polyion–Counterion Interaction Parameter (f). The polyion–counterion interaction parameter, f , which, as pointed out earlier, can also be looked at as the fraction of uncondensed counterions, can be obtained from eq 2 using the measured equivalent conductance in conjunction with the λ_p value obtained theoretically from eq 4 and the λ_c^0 value of the counterion. This f corresponds to the actual interaction between a polyion and counterions prevailing in solution. A representative plot depicting the variation of f with the square root of concentration at a given temperature in acetonitrile/water mixed-solvent media is given in Figure 5. This parameter (f) can also be calculated from

TABLE 2: Calculated (from Eq 1) and Best-Fitted Charge-Density Parameter, ξ , in Acetonitrile/Water Mixtures at 308.15, 313.15, and 318.15 K

acetonitrile	ξ value at $T = 308.15$ K		ξ value at $T = 313.15$ K		ξ value at $T = 318.15$ K	
	calcd ^a	best fitted (sd ^b)	calcd ^a	best fitted (sd ^b)	calcd ^a	best fitted (sd ^b)
10%	1.0242	1.42(1.32)	1.0405	1.46(4.03)	1.0484	1.48(2.70)
20%	1.0877	1.57(1.09)	1.0955	1.50(2.15)	1.1039	1.52(1.83)
40%	1.2302	1.59(1.82)	1.2416	1.77(1.59)	1.2487	1.84(2.98)

^a Obtained assuming a fully stretched polyion. ^b Standard deviation of fit.

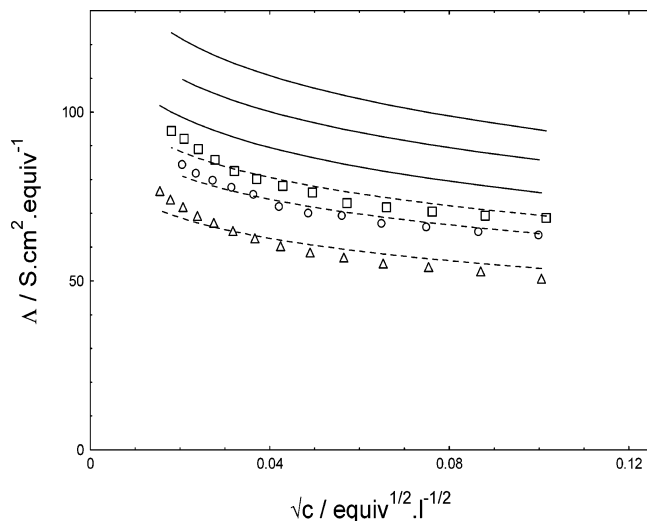


Figure 4. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaCMC with those predicted by the Manning theory at 308.15 K. Experimental values: squares, 10% acetonitrile; circles, 20% acetonitrile; triangles, 40% acetonitrile. Calculated with structural ξ : solid lines for 10, 20, and 40% acetonitrile respectively from top to bottom. Calculated with best-fitted ξ : broken lines.

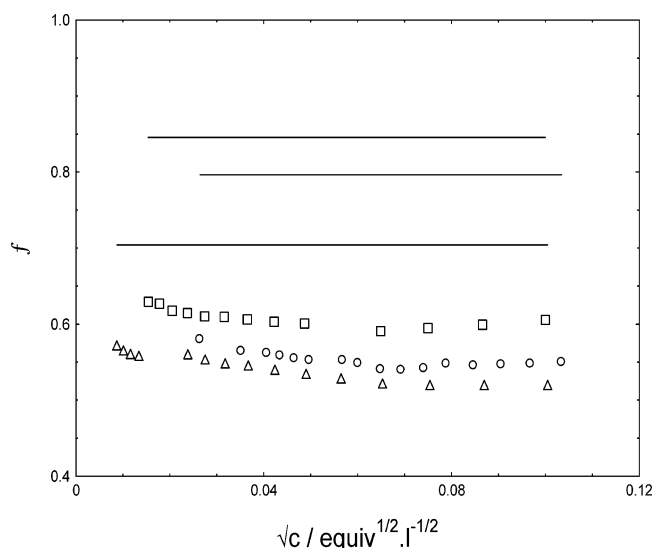


Figure 5. Dependence of the calculated values of the fraction of uncondensed counterions, f , on the square root of the polymer concentration (\sqrt{c}) in various acetonitrile/water mixtures at 308.15 K. Experimental (from eq 2): squares, 10% acetonitrile; circles, 20% acetonitrile; triangles, 40% acetonitrile. Calculated from eq 3: solid lines, 10, 20, and 40% acetonitrile respectively from top to bottom.

purely theoretical considerations (eq 3) using a charge-density parameter, ξ , assuming a fully stretched conformation of the polyion chain given in Table 2. These two estimates of f differ appreciably; eq 3 always predicts higher values than eq 2 does. We have also included the predictions by eq 3 in Figure 5 (lines).

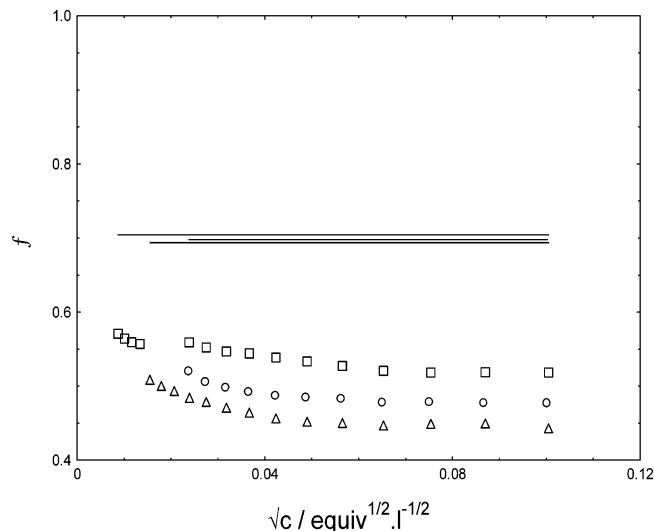


Figure 6. Dependence of the calculated values of the fraction of uncondensed counterions, f , on the square root of the polymer concentration (\sqrt{c}) at various temperatures in 40% acetonitrile/water mixtures. Experimental: squares, 308.15 K; circles, 313.15 K; triangles, 318.15 K. Calculated from eq 3: solid lines, 308.15, 313.15, and 318.15 K respectively from top to bottom.

A comparison shows that the polyions are subjected to stronger interactions with the counterions and definite concentration dependence as compared to the prediction by eq 3. This observation seems to indicate that the evaluation of f on the basis of eq 3 does not appear to be correct. This probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies eq 3.

The measured fraction of uncondensed counterions is found to decrease with decreasing relative permittivity (i.e., with increasing acetonitrile content of the mixed-solvent media) at each temperature (Figure 5) because decreasing relative permittivity should result in a greater interaction between the polyion and counterions, which, in turn, would enhance the fraction of condensed counterions.

The influence of temperature on the f value in different mixed-solvent media is, at first sight, rather perplexing. Figure 6 shows an f versus the square root of polyelectrolyte concentration plot in 40% acetonitrile at different temperatures in a representative manner. For any given mixed-solvent system, the fraction of uncondensed counterions is found to decrease with increasing temperature, which apparently contradicts the observation in Figures 1–3, where Λ increases with temperature in each of the mixed-solvent media investigated. This can be ascribed to a change in the solvation and condensation behavior of the counterions upon changing the temperature. Raising the temperature has the effect of decreasing ionic solvation for the counterions, 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. Still, the equivalent conductivities increase with increasing temper-

ature because of a temperature-induced increase in the speed of the ions in a lower-viscosity medium at higher temperatures.

4. Conclusions

Experimental results for the equivalent conductivity of a salt-free solution of a polyelectrolyte NaCMC in acetonitrile/water mixed-solvent media have been presented as a function of the polymer concentration and temperature. The equivalent conductivities are found to increase with increasing temperature over the entire concentration range in a given mixed-solvent medium, whereas these values 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 equivalent conductivity cannot be quantitatively described by this theory. The discrepancies may be attributed to many simplifying assumptions made in the theoretical model under examination. The ion-ion correlations have not been included in this theory; these interactions must necessarily lead to deviation from the theory. The polyion is not an infinitely long cylinder as assumed in this theory. Further, the model ignores the molecular nature of the solvent and dielectric discontinuity at the polyion-solution boundary. In addition, this theory ascribes all of the deviations from the ideality to the electrostatic counterion-polyion interaction, which, in reality, may not be the case. Specific interactions that are not related to the electrostatic interaction of counterions and macroions could also be responsible for the discrepancy between the electrostatic theory and the experimental results.

References and Notes

- (1) Mandel, M. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley & Sons: New York, 1988; Vol. 11, p 739.
- (2) Leeuwen, H. P. V.; Cleven, R. F. M.; Valenta, P. *Pure Appl. Chem.* **1991**, *63*, 1251.
- (3) Wandrey, C. *Polyelektrolyte-Makromolekulare Parameter und Elektrolytverhalten*; Cuvillier Verlag: Göttingen, Germany, 1997.
- (4) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
- (5) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
- (6) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
- (7) Manning, G. S. *J. Phys. Chem.* **1975**, *79*, 262.
- (8) Manning, G. S. *J. Phys. Chem.* **1981**, *85*, 1506.
- (9) Oosawa, F. *Polyelectrolyte*; Marcel Dekker: New York, 1971.
- (10) Manning, G. S. *Biopolymers* **1970**, *9*, 1543.
- (11) Huizenga, J. R.; Grieger, P. F.; Wall, F. T. *J. Am. Chem. Soc.* **1950**, *72*, 2636.
- (12) Barraza, R. G.; Rios, H. E. *Polym. Int.* **1975**, *38*, 387.
- (13) Abramovic, H.; Klotfutar, C. *Eur. Polym. J.* **1997**, *33*, 1295.
- (14) Hara, M. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993; pp 202–205.
- (15) Moumouzias, G.; Panopoulos, D. K.; Ritzoulis, G. *J. Chem. Eng. Data* **1991**, *36*, 20.
- (16) Pal, M.; Bagchi, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 961.
- (17) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth: London, 1959.
- (18) Moreau, C.; Douheret, G. *J. Chem. Thermodyn.* **1976**, *8*, 403.
- (19) Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1557.
- (20) Ghosh, D.; Das, D. *J. Chem. Eng. Data* **2004**, *49*, 1771.
- (21) Ward, K., Jr.; Seib, P. A. In *The Carbohydrates, Chemistry and Biochemistry*; Pigwan, W., Horton, D., Eds.; Academic Press: New York, 1970; Vol. 2A, p 420.
- (22) Kwak, J. C. T.; Johnston, A. J. *Can. J. Chem.* **1975**, *53*, 792.
- (23) Rios, H. E.; Barraza, R. G.; Gamboa, I. C. *Polym. Int.* **1993**, *31*, 213.
- (24) Rios, H. E. *Polym. Int.* **2001**, *50*, 885.
- (25) Szymczak, J.; Holyk, P.; Ander, P. *J. Phys. Chem.* **1975**, *79*, 269.
- (26) Abramovic, H.; Klotfutar, C. *Eur. Polym. J.* **1997**, *33*, 1295.
- (27) Katchalsky, A. *Pure Appl. Chem.* **1971**, *26*, 327.
- (28) Manning, G. S. *J. Phys. Chem.* **1984**, *88*, 6654.
- (29) Dolar, D. In *Polyelectrolytes*; Sélegny, E., Mandel, M., Strauss, U. P., Eds.; D. Reidel: Dordrecht, The Netherlands, 1974; p 97.
- (30) Jiang, J.; Liu, H.; Hu, Y. *J. Chem. Phys.* **1999**, *110*, 4952.
- (31) Lamm, G.; Pack, G. R. *J. Phys. Chem. B* **1997**, *101*, 959.