Chapter IV

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

Introduction

In accounting for the solution behaviour 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 behaviour of neutral polymers caused by the existence of charges along the polymer chain and deviation from the behaviour 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 behaviour 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]

$$\xi = \frac{e^2}{bDk_BT} \tag{1}$$

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 Boltzman constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions

condense on to 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]

$$\Lambda = f(\lambda_c^0 + \lambda_p) \tag{2}$$

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 counterion–polyion interaction parameter given by[4,6,9]

$$f = \frac{0.866}{\xi} \tag{3}$$

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-Hückel 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

$$\lambda_p = \frac{279 A |z_c|^{-1} |\ln \kappa a|}{1 + 43.2 A(|z_c| \lambda_c^0)^{-1} |\ln \kappa a|} \tag{4}$$

where the parameter a is the radius of the polymer chain, while

$$A = \frac{D k_B T}{3 \pi \eta_0 e} \tag{5}$$

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with η_0 being the coefficient of viscosity of the solvent. In Eq. (4), κ is the Debye screening constant, which is defined by

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

where n_e 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 section, the results are reported for conductivity measurements on the 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 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.

Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentaoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 gm.cm^{-3} and a co-efficient 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 less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents. The physical properties namely the the coefficients of viscosities (η_0) and the relative permittivities (D) of acetonitrile-water mixed solvents used in this study at experimental temperatures are reported in Table 1. The relative permittivities of 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 2 of the

previous chapter. 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 acetonitrile, and the permittivity values were generated from the smooth master plot; these values are found to be in good agreement with our values.

NaCMC was purchased from Aldrich Chemical Co., Inc. The average molecular weight (M_w) of the sample was 90 000 with a degree of substitution (DS) of 0.70, and these values agree well with those obtained from physicochemical 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 percent. 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 ± 0.005 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.

Result and Discussion

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 behaviour, 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 volume percent acetonitrile-water mixtures over the entire concentration range investigated. This is expected because as the relative permittivity of the medium decreases, interaction between 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.

Comparison with Manning Counterion Condensation Theory

Now we will compare the experimental values 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 volume percent of acetonitrile mixtures were taken from the literature,[22] while those in the 10 volume percent 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 length[21] of 5.15 $\overset{0}{\text{A}}$, 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 change in concentration dependence of λ_p upon varying a between realistic values is small. A cylindrical radius of 7 $\overset{0}{\text{A}}$ was used for the present analysis.[22]

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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 (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 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 towards 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 the 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 experiment and theoretical values include deviation from the rod like 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 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 polyion of finite length.

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 λ_c^0 value of the counterion. This f corresponds to the actual interaction between polyion and counterions prevailing in solution. A represantative plot depicting the variation of f with the square root of concentration at a given temperasture in acetonitrile-water mixed solvent media is given in Figure 5. This parameter (f) can also be calculated from purely theoretical considerations, Eq. (3), using a charge density parameter, ξ, assuming fully stretched conformation of the polyion chain given in Table 2. These two estimates of f differ appreciably; Eq. (3) always predicts the higher values than Eq. (2) does. We have also included the predictions by Eq. (3) in Figure 5 (lines).

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 volume percent 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 medium investigated. This can be ascribed to a change in solvation and condensation behaviour 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 temperature because of a temperature-induced increase in the speed of the ions in a lower-viscosity medium at higher temperatures.

Conclusions

Experimental results for the equivalent conductivity of salt-free solution of a polyelectrolyte NaCMC in acetonitrile-water mixed solvent media have been presented as a function of 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 can not 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 also dielectric

discontinuity at the polyion-solution boundary. In addition this theory ascribes all the deviations from the ideality to the 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 experiment.

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Table 1. Coefficients of Viscosities, η_0 (mPa.s), Relative Permittivities (D) and the Corresponding Limiting Ionic Equivalent Conductivities of the Counterion, λ^0_c (S.cm^2.mol^{-1}) of Acetonitrile-Water Mixtures Containing 10, 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

T (K)	η_0 (mPa.s)	D	λ^0_c (S.cm^2.mol^{-1})
	10 Vol% 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 Vol% 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 Vol% 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

Table 2. Calculated, from Eq. (1), and Best Fitted Charge Density Parameters (ξ) in Acetonitrile-Water Mixtures at 308.15, 313.15, and 318.15 K

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

[a] Obtained assuming fully stretched polyion.

[b] standard deviation of fit
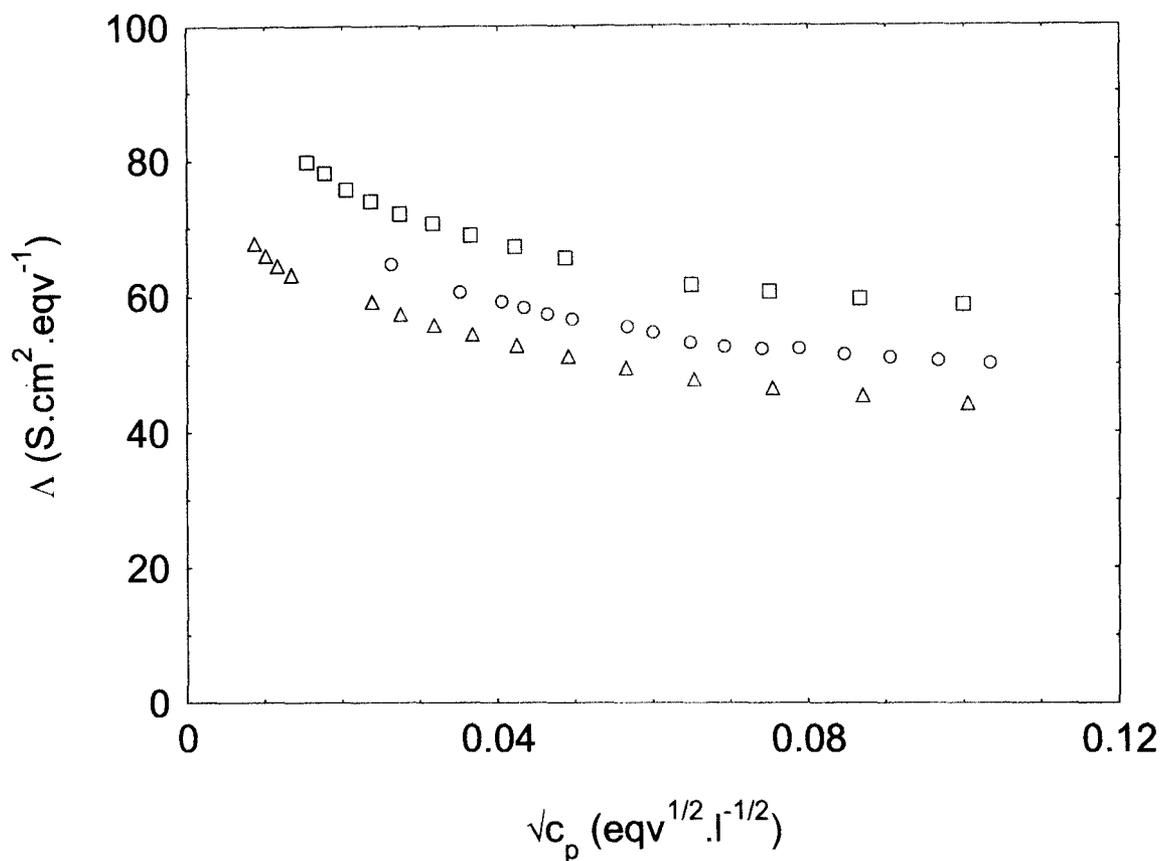
Figure 1. Equivalent conductivities (Λ) of NaCMC as a function of square root of the polymer concentration ($\sqrt{c_p}$) at the temperature of 308.15 K, in different acetonitrile-water mixtures: 10 volume percent acetonitrile, Squares; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Tringles.
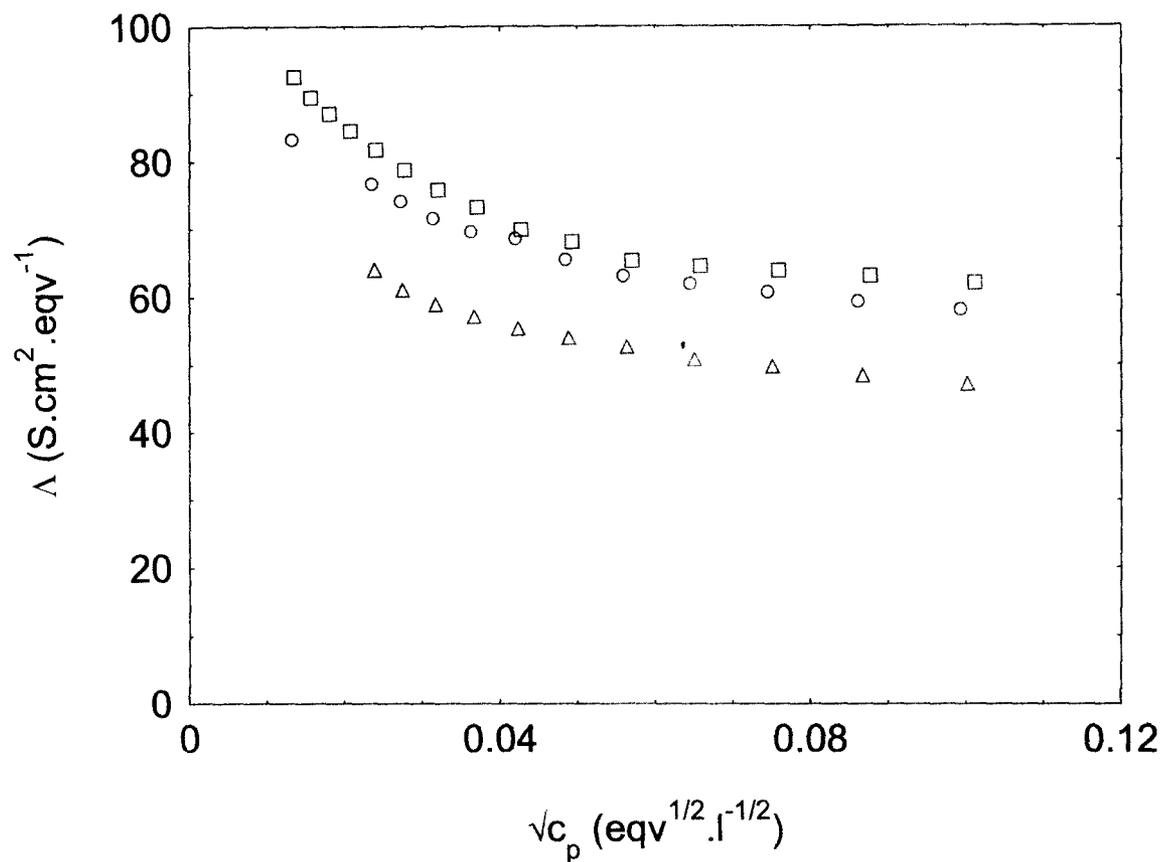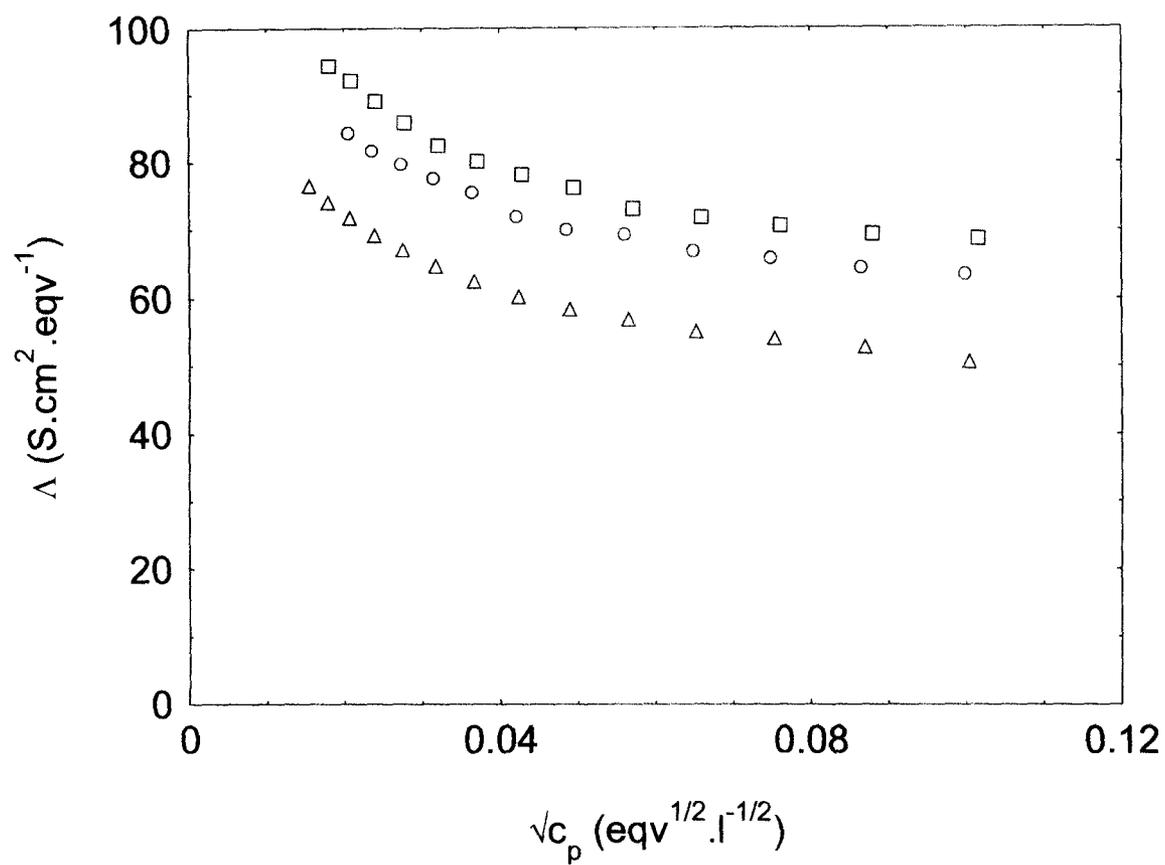
Figure 2. Equivalent conductivities (Λ) of NaCMC as a function of square root of the polymer concentration ($\sqrt{c_p}$) at the temperature of 313.15 K, in different acetonitrile-water mixtures: 10 volume percent acetonitrile, Squares; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Tringles.
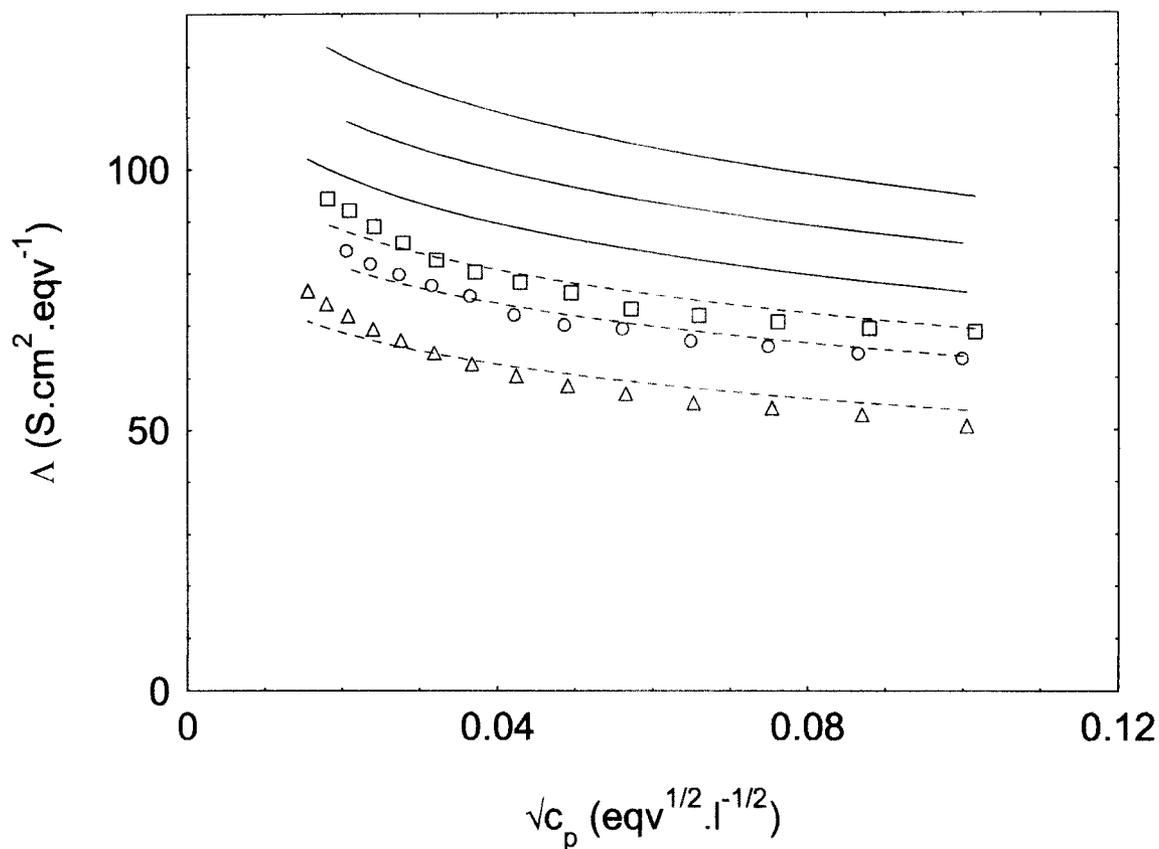
Figure 3. Equivalent conductivities (Λ) of NaCMC as a function of square root of the polymer concentration ($\sqrt{c_p}$) at the temperature of 318.15 K, in different acetonitrile-water mixtures: 10 volume percent acetonitrile, Squares; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Tringles.

Figure 4. Comparison of the experimental values of the equivalent conductivity (Λ) of solutions of NaCMC with those predicted by Manning theory at 318.15 K: Experimental values: 10 volume percent acetonitrile, Squares; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Tringles.; Calculated with structural ξ: solid lines for 10 20 and 40 volume percent acetonitrile respectively from top to bottom; Calculated with best fitted ξ: broken lines.
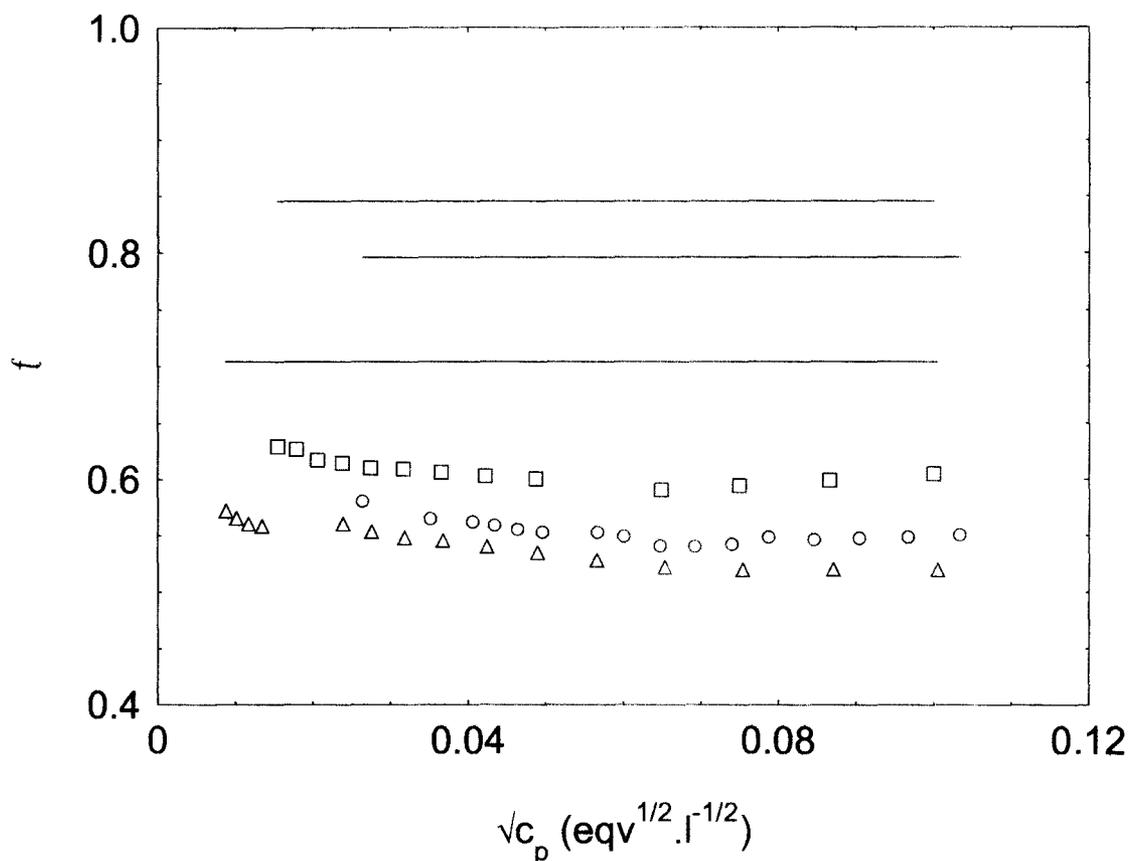
Figure 5: Dependence of the calculated values of the fraction of uncondensed counterions, f, on the square root of the polymer concentration ($\sqrt{c_p}$) in various acetonitrile-water mixtures at 308.15 K: Experimental, from Eq. (2): 10 volume percent acetonitrile, Squares; 20 volume percent acetonitrile, Circles; 40 volume percent acetonitrile, Tringles.; Calculated from Eq. (3): solid lines, 10, 20, and 40 volume percent acetonitrile respectively from top to bottom.
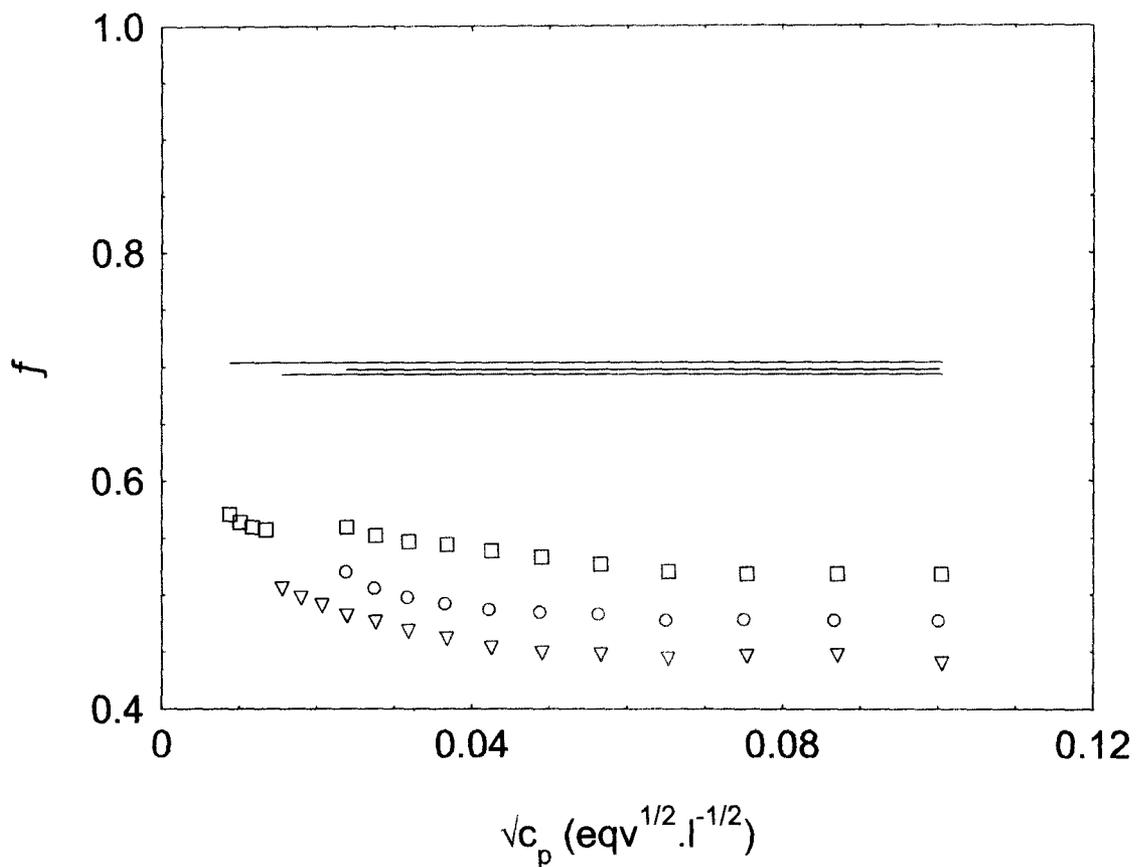
Figure 6. Dependence of the calculated values of the fraction of uncondensed counterions, f, on the square root of the polymer concentration ($\sqrt{c_p}$) at various temperatures in 40 volume percent acetonitrile-water mixtures: Experimental: 308.15 K, Squares; 313.15 K, Circles; and 318.15 K, Triangles; Calculated from Eq. (3): solid lines, 308.15, 313.15, and 318.15 K respectively from top to bottom.