

Electrical Conductances of Sodium Carboxymethylcellulose in Acetonitrile (1) + Water (2) Mixed Solvent Media in the Presence of Sodium Chloride at 308.15 K

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ABSTRACT: The electrical conductances of solutions of an anionic polyelectrolyte sodium carboxymethylcellulose in acetonitrile (1) + water (2) mixed solvent media containing 0.10, 0.20, and 0.40 volume fractions of acetonitrile (v_1) have been reported at 308.15 K in the presence of sodium chloride. The conductance data have been analyzed on the basis of an equation recently developed by us (*J. Chem. Eng. Data*, 2010, 55, 2108–2115) following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a polyion chain according to Dobrynin et al. (*Macromolecules*, 1995, 28, 1859–1871). Excellent quantitative agreement between the experimental results and those obtained using the equation developed here was observed. This provides further support in favor of the approach developed. Influences of the solvent composition and the concentration of the added salt were also examined.

INTRODUCTION

We have reported the results of conductivity measurements on salt-free solutions of sodium carboxymethylcellulose in acetonitrile (1) + water (2) mixtures in an earlier communication.¹ The addition of salts to a polyelectrolyte solution might change its conductivity behavior considerably, and hence studies on the conductivity of polyelectrolytes in the presence of a salt might help elucidate polyion–counterion interactions in polyelectrolytes with added salts.

Although the polyelectrolyte conductivities have been well-understood in salt-free solutions² using the scaling description for the configuration of a polyion chain according to Dobrynin et al.,³ the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning⁴ first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory⁵ without much success. In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the “primitive additivity”) of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.^{6–10}

Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_p + \kappa_s \quad (1)$$

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_s is the specific conductance of the simple salt in the absence of a polyelectrolyte.

However, these investigations^{6–10} suggest that the experimentally obtained specific conductances for salt-containing

polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, eq 1.

Ander et al.^{6,7} modified the “primitive” additivity by taking into account the Debye–Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte–salt solution as

$$\kappa = \kappa_p + \kappa_s \left(\frac{D_2}{D_2^0} \right) \quad (2)$$

where D_2 and D_2^0 are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2/D_2^0 has been used as a quantitative measure⁵ of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s(D_2/D_2^0)$.

Although the “modified” additivity has been shown to be somewhat better than the “primitive” one, departures from the experimental results are still prominent.^{6–10} Later Bordi et al.¹¹ evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach³ and compared them with the experimentally determined values. The agreement was rather good, although a quantitative description was not achieved.

Very recently, a simple approach has been put forward by us¹² to analyze the conductivity of polyelectrolyte solutions in the presence of an added electrolyte following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby et al.² using the scaling description for the configuration of a polyion chain according to Dobrynin et al.³ This approach has been extensively tested with data on sodium polystyrenesulfonate in the presence of sodium chloride in

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2-ethoxyethanol (1) + water (2) mixed solvent media at different temperatures.¹² The data set used considered a number of parameters, for example, relative permittivity of the medium, temperature, and concentration of the added salt. Moreover, three decades of concentration of the polyelectrolyte were covered. Very good quantitative agreement with only one adjustable parameter has been observed.

In this paper, we report the results of conductivity measurements on the solutions of another polyelectrolyte sodium carboxymethylcellulose in the presence of sodium chloride in acetonitrile (1) + water (2) mixtures. The goal of this communication is to apply this new approach to a different polyelectrolyte–solvent system to test its general validity and to examine the influences of the medium and the concentration of the added salt on the counterion-condensation behavior of the polyelectrolyte in the presence of a salt.

THEORY

Here we briefly review the model recently introduced by us to describe the conductivity behavior of polyelectrolyte in salt solutions.¹²

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 $q_{\xi} = zefg$ (z being the counterion valence and e is the electronic charge), and the complete chain, of contour length $L = N_{\xi}\xi_0$, bears a charge $Q_p = N_{\xi}q_{\xi} = zefgN_{\xi}$, where f is the fraction of uncondensed counterions. Because of 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 electrostatic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Following Colby et al.,² the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

$$\kappa_p = fc \left[\lambda_c^0 + \frac{c\xi_0^2 e^2 f}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (3)$$

where c is the number density of monomers, λ_c^0 the limiting equivalent conductivity of the counterions, and η_0 the coefficient of the viscosity of the medium.

The interactions between the polyion and the counterions will be modified in the presence of an electrolyte and this will result in a different level of counterion condensation, that is, in a different value of f (designated as f'). The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt can be expressed as

$$\kappa_{p(\text{eff})} = f'c \left[\lambda_c^0 + \frac{c\xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (4)$$

Thus, the total specific conductivity (κ) of a polyelectrolyte solution with added simple electrolyte should be equal to the sum of the specific conductivity of the simple salt in the absence of a polyelectrolyte and the effective specific conductivity due to the

Table 1. Properties of Acetonitrile (1) + Water (2) Mixtures Containing 0.10, 0.20, and 0.40 Volume Fractions of Acetonitrile, the Charge Density Parameters (ξ), and the Corresponding Limiting Ionic Equivalent Conductivities of the Sodium Ion (λ_c^0) at 308.15 K

| volume fraction | η_0 | ε | ξ | $10^4 \lambda_c^0$ |
|-----------------|----------|---------------|--------|------------------------------|
| (v_1) | mPa·s | | | $S \cdot m^2 \cdot eqv^{-1}$ |
| 0.10 | 0.8766 | 72.15 | 1.0242 | 58.81 |
| 0.20 | 0.9067 | 67.94 | 1.0877 | 56.21 |
| 0.40 | 0.8200 | 60.07 | 1.2302 | 51.50 |

polyelectrolyte in the presence of a simple salt and is given by

$$\kappa = \kappa_s + f'c \left[\lambda_c^0 + \frac{c\xi_0^2 e^2 f'}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (5)$$

This equation (eq 5) has one adjustable parameter f' , and this could be obtained by the method of a least-squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in the presence of a salt to eq 5 using the measured specific conductance (κ_s) of the salt in the absence of the polyelectrolyte. This value of f' takes care of the changed polyion–counterion interactions under the influence of the added salt. The second term in eq 5 is the actual contribution of the polyelectrolyte species toward the total specific conductivity in the presence of an added salt.

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 $765.70 \text{ kg} \cdot \text{m}^{-3}$ and a coefficient of viscosity of $0.3126 \text{ mPa} \cdot \text{s}$ at 308.15 K; these values are in good agreement with literature values.¹³ Triply distilled water with a specific conductance of about $10^{-4} \text{ S} \cdot \text{m}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of acetonitrile (1) + water (2) mixtures at 308.15 K, namely, the coefficients of viscosity (η_0) and the relative permittivities (ε), were obtained from our earlier paper¹ and are reported in Table 1. Also included in this table are the limiting ionic equivalent conductivities of the sodium ion (λ_c^0) in acetonitrile (1) + water (2) mixtures at 308.15 K.¹

Sodium carboxymethylcellulose used in these investigations was purchased from Aldrich Chemicals. The average molecular weight (M_w) of the sample was 90 000 with a degree of substitution (DS) of 0.70. The average molecular weight of the sample was also estimated from the intrinsic viscosity value determined in 0.2 M NaCl aqueous solution at 298.15 K using the Mark–Houwink equation with the constants obtained from the literature.¹⁴ DS was determined by a conductometric procedure as described by Eyler et al.¹⁵ These values agree well with those declared by the producer.

Sodium chloride (Fluka) was of puriss grade. This was dried in vacuo for a prolonged period immediately before use and was used without further purification.

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 115 m^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers¹⁶ using aqueous potassium chloride

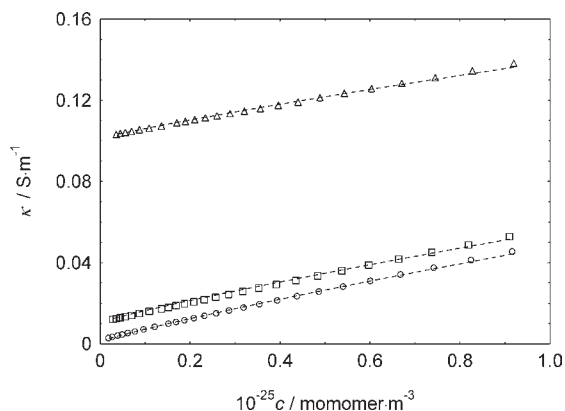


Figure 1. Specific conductivities of sodium carboxymethylcellulose as a function of the number density of monomers (c) at 308.15 K in an acetonitrile (1) + water (2) mixture with $v_1 = 0.10$. Experimental: Open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.1, 1.0, and 10.0) $\text{mol} \cdot \text{m}^{-3}$ of NaCl, respectively.

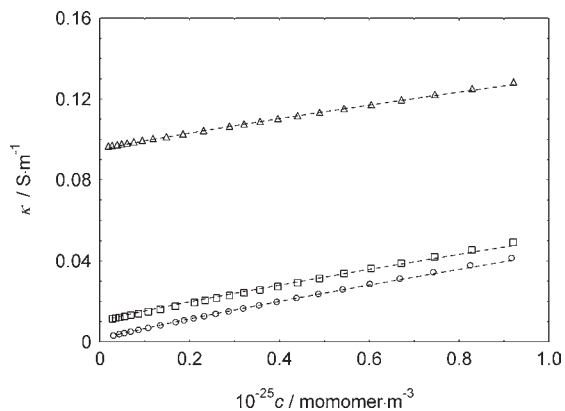


Figure 2. Specific conductivities of sodium carboxymethylcellulose as a function of the number density of monomers (c) at 308.15 K in an acetonitrile (1) + water (2) mixture with $v_1 = 0.20$. Experimental: Open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.1, 1.0, and 10.0) $\text{mol} \cdot \text{m}^{-3}$ of NaCl, respectively.

solution. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. The details of the experimental procedure have been described earlier.^{17,18} Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results.

To avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates. The experimental uncertainties in the conductivity measurements were always found to be within 0.3 %.

RESULTS AND DISCUSSION

The experimental values of specific conductivities (κ) of sodium carboxymethylcellulose in the presence of varying concentrations of sodium chloride ((0.1, 1.0, and 10.0) $\text{mol} \cdot \text{m}^{-3}$) in acetonitrile (1) + water (2) mixtures have been listed as a

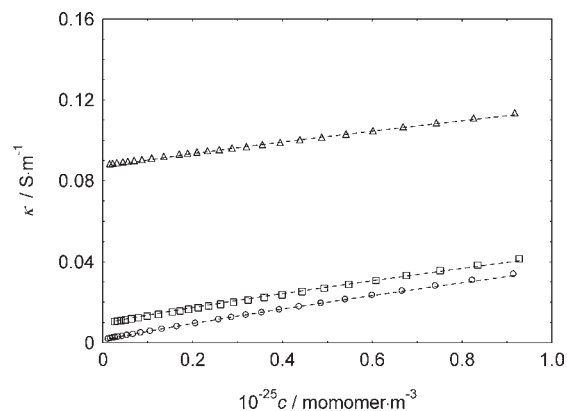


Figure 3. Specific conductivities of sodium carboxymethylcellulose as a function of the number density of monomers (c) at 308.15 K in an acetonitrile (1) + water (2) mixture with $v_1 = 0.40$. Experimental: Open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.1, 1.0, and 10.0) $\text{mol} \cdot \text{m}^{-3}$ of NaCl, respectively.

function of the number density of monomers (c) at 308.15 K in Table 2. The specific conductivities of sodium carboxymethylcellulose as a function of the polymer concentration in a given solvent composition in acetonitrile (1) + water (2) mixtures with varying amounts of added NaCl are shown in representative Figures 1 through 3. From these figures and also from Table 2, it is apparent that for all of the solutions studied the specific conductivities increase with polyelectrolyte concentration. The addition of salt increases the specific conductances of the polyelectrolyte–salt solutions as expected. The specific conductances of the polyelectrolyte–salt systems are, in general, found to decrease with increasing amount of acetonitrile in the mixed solvent media at constant salinity (cf. Table 2).

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) appearing in eq 5 depend upon the quality of the solvent and are, for poor solvents, given by²

$$\xi_e = b(\xi f'^2)^{-1/3} \quad (6)$$

$$\xi_0 = (cb)^{-1/2}(\xi f'^2)^{-1/3} \quad (7)$$

with the charge density parameter ξ defined as

$$\xi = \frac{e^2}{\epsilon k T b} \quad (8)$$

where b is the spacing between the charged groups taken along the axis of the polyion chain, k the Boltzmann constant, and T the temperature in absolute scale. The charge density parameters were calculated using a segment length of $5.15 \cdot 10^{-10}$ m, considering a degree of substitution of 0.70, and these are included in Table 1.

For good solvent cases, on the other hand, these are given by²

$$\xi_e = b(\xi f'^2)^{-3/7} \quad (9)$$

$$\xi_0 = (cb)^{-1/2}(\xi f'^2)^{-1/7} \quad (10)$$

For the present system, poor solvent correlations are always found to provide a better description of the experimental results.

Table 2. Specific Conductance Values of Sodium Carboxymethylcellulose in the Presence of NaCl in Acetonitrile (1) + Water (2) Mixed Solvent Media at 308.15 K

| $c_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{m}^{-3}$ | | $c_{\text{NaCl}} = 1.0 \text{ mol} \cdot \text{m}^{-3}$ | | $c_{\text{NaCl}} = 10.0 \text{ mol} \cdot \text{m}^{-3}$ | |
|---|--------------------------------|---|--------------------------------|--|--------------------------------|
| $10^{-25} c$ | $10^4 \kappa$ | $10^{-25} c$ | $10^4 \kappa$ | $10^{-25} c$ | $10^4 \kappa$ |
| momomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ | momomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ | momomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ |
| $\nu_1 = 0.10$ | | | | | |
| 0.91722 | 452.0 | 0.91013 | 528.0 | 0.91961 | 1378.0 |
| 0.82551 | 410.0 | 0.81912 | 488.0 | 0.82764 | 1341.0 |
| 0.74296 | 372.0 | 0.73721 | 451.0 | 0.74489 | 1307.0 |
| 0.66866 | 339.0 | 0.66349 | 418.0 | 0.67039 | 1279.0 |
| 0.60180 | 307.0 | 0.59714 | 388.0 | 0.60335 | 1253.0 |
| 0.54162 | 279.0 | 0.53743 | 360.0 | 0.54302 | 1230.0 |
| 0.48746 | 254.5 | 0.48369 | 335.0 | 0.48872 | 1208.0 |
| 0.43871 | 231.4 | 0.43531 | 312.0 | 0.43985 | 1187.0 |
| 0.39484 | 211.2 | 0.39178 | 292.2 | 0.39586 | 1171.0 |
| 0.35536 | 192.6 | 0.35261 | 273.8 | 0.35627 | 1155.0 |
| 0.31982 | 176.0 | 0.31735 | 257.8 | 0.32065 | 1142.0 |
| 0.28784 | 161.1 | 0.28561 | 242.9 | 0.28858 | 1130.0 |
| 0.25905 | 147.2 | 0.25704 | 229.2 | 0.25972 | 1119.0 |
| 0.23315 | 134.9 | 0.23135 | 217.3 | 0.23375 | 1109.0 |
| 0.20984 | 123.6 | 0.20821 | 206.5 | 0.21038 | 1100.0 |
| 0.18885 | 113.4 | 0.18739 | 196.7 | 0.18933 | 1091.0 |
| 0.16997 | 104.4 | 0.16865 | 187.9 | 0.17040 | 1084.0 |
| 0.15297 | 96.0 | 0.15179 | 179.9 | 0.13632 | 1069.0 |
| 0.12238 | 80.7 | 0.13661 | 172.6 | 0.10906 | 1058.0 |
| 0.09790 | 68.2 | 0.10928 | 159.6 | 0.08725 | 1050.0 |
| 0.07832 | 58.0 | 0.08743 | 148.9 | 0.06980 | 1042.0 |
| 0.06266 | 49.8 | 0.06994 | 140.3 | 0.05584 | 1037.0 |
| 0.05013 | 43.0 | 0.05595 | 133.5 | 0.04467 | 1032.0 |
| 0.04010 | 37.6 | 0.04476 | 128.1 | 0.03574 | 1027.0 |
| 0.02807 | 30.7 | 0.03581 | 123.5 | 0 | 1011.0 |
| 0.01965 | 25.9 | 0.02865 | 120.3 | | |
| 0 | 12.2 | 0 | 106.2 | | |
| $\nu_1 = 0.20$ | | | | | |
| 0.91808 | 412.0 | 0.92040 | 492.0 | 0.92118 | 1280.0 |
| 0.82622 | 375.0 | 0.82836 | 454.0 | 0.82906 | 1248.0 |
| 0.74360 | 342.0 | 0.74552 | 420.0 | 0.74616 | 1219.0 |
| 0.66924 | 310.0 | 0.67097 | 389.0 | 0.67154 | 1192.0 |
| 0.60232 | 282.3 | 0.60387 | 362.3 | 0.60439 | 1168.0 |
| 0.54209 | 256.9 | 0.54349 | 337.9 | 0.54395 | 1149.0 |
| 0.48788 | 234.4 | 0.48913 | 313.4 | 0.48955 | 1130.0 |
| 0.43909 | 213.7 | 0.44023 | 292.2 | 0.44060 | 1113.0 |
| 0.39518 | 194.6 | 0.39620 | 273.5 | 0.39654 | 1099.0 |
| 0.35567 | 177.5 | 0.35658 | 256.9 | 0.35688 | 1085.0 |
| 0.32010 | 162.0 | 0.32092 | 241.8 | 0.32119 | 1072.0 |
| 0.28809 | 147.7 | 0.28883 | 228.3 | 0.28908 | 1062.0 |
| 0.25927 | 135.1 | 0.25994 | 216.0 | 0.23126 | 1040.0 |
| 0.23336 | 123.5 | 0.23395 | 204.9 | 0.18501 | 1023.0 |
| 0.21001 | 112.8 | 0.21055 | 194.6 | 0.14801 | 1009.0 |
| 0.18901 | 103.2 | 0.16844 | 176.0 | 0.11841 | 1000.0 |
| 0.17011 | 94.7 | 0.13476 | 160.9 | 0.09473 | 991.0 |
| 0.13608 | 78.9 | 0.10780 | 148.9 | 0.07578 | 984.0 |
| 0.10888 | 66.0 | 0.08624 | 139.4 | 0.06062 | 978.0 |
| 0.08709 | 55.6 | 0.06900 | 132.0 | 0.04850 | 974.0 |

Table 2. Continued

| $c_{\text{NaCl}} = 0.1 \text{ mol} \cdot \text{m}^{-3}$ | | $c_{\text{NaCl}} = 1.0 \text{ mol} \cdot \text{m}^{-3}$ | | $c_{\text{NaCl}} = 10.0 \text{ mol} \cdot \text{m}^{-3}$ | |
|---|--------------------------------|---|--------------------------------|--|--------------------------------|
| $10^{-25} c$ | $10^4 \kappa$ | $10^{-25} c$ | $10^4 \kappa$ | $10^{-25} c$ | $10^4 \kappa$ |
| monomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ | monomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ | monomer $\cdot \text{m}^{-3}$ | $\text{S} \cdot \text{m}^{-1}$ |
| 0.06968 | 47.2 | 0.05520 | 126.0 | 0.03880 | 970.0 |
| 0.05574 | 40.5 | 0.04416 | 121.2 | 0.02716 | 966.0 |
| 0.04459 | 35.0 | 0.03533 | 117.3 | 0.01901 | 963.0 |
| 0.03122 | 28.4 | 0.02826 | 114.3 | 0 | 947.0 |
| 0 | 12.1 | 0 | 100.7 | | |
| $\nu_1 = 0.40$ | | | | | |
| 0.91489 | 338.0 | 0.92750 | 415.0 | 0.91724 | 1132.0 |
| 0.82339 | 308.0 | 0.83475 | 384.0 | 0.82551 | 1106.0 |
| 0.74104 | 280.1 | 0.75127 | 357.0 | 0.74296 | 1083.0 |
| 0.66694 | 255.4 | 0.67614 | 332.0 | 0.66866 | 1063.0 |
| 0.60025 | 233.2 | 0.60853 | 308.0 | 0.60180 | 1044.0 |
| 0.54023 | 212.9 | 0.54768 | 288.0 | 0.54162 | 1027.0 |
| 0.48619 | 194.2 | 0.49292 | 269.2 | 0.48746 | 1011.0 |
| 0.43758 | 177.5 | 0.44362 | 252.7 | 0.43871 | 999.0 |
| 0.39382 | 162.4 | 0.39926 | 237.2 | 0.39484 | 986.0 |
| 0.35444 | 148.3 | 0.35933 | 223.8 | 0.35536 | 975.0 |
| 0.31899 | 135.9 | 0.32340 | 211.2 | 0.31982 | 965.0 |
| 0.28709 | 124.4 | 0.29106 | 200.3 | 0.28784 | 958.0 |
| 0.25839 | 114.2 | 0.26195 | 190.2 | 0.25905 | 950.0 |
| 0.20671 | 94.9 | 0.23576 | 180.8 | 0.23315 | 944.0 |
| 0.16537 | 79.4 | 0.21218 | 172.4 | 0.20984 | 938.0 |
| 0.13230 | 66.8 | 0.19096 | 164.8 | 0.18885 | 932.0 |
| 0.10583 | 56.6 | 0.17187 | 158.0 | 0.16997 | 928.0 |
| 0.08467 | 48.0 | 0.15468 | 151.8 | 0.13598 | 917.0 |
| 0.06773 | 41.3 | 0.12374 | 140.7 | 0.10878 | 908.0 |
| 0.05419 | 35.8 | 0.09899 | 131.4 | 0.08702 | 901.0 |
| 0.04335 | 31.4 | 0.07920 | 124.1 | 0.06962 | 896.0 |
| 0.03468 | 28.0 | 0.06336 | 118.3 | 0.05569 | 891.0 |
| 0.02774 | 24.9 | 0.05069 | 113.7 | 0.04456 | 889.0 |
| 0.02219 | 22.4 | 0.04055 | 110.0 | 0.03119 | 885.0 |
| 0.01776 | 20.4 | 0.03244 | 106.9 | 0.02183 | 882.0 |
| 0.01243 | 18.1 | 0.02595 | 104.5 | 0.01528 | 880.0 |
| 0 | 10.7 | | 93.2 | 0 | 865.0 |

In Figures 1 to 3, the predictions in accordance with eq 5 (dashed lines) have been compared with the experimental specific conductivity data treating the mixed solvent media as a poor solvent for sodium carboxymethylcellulose.

The specific conductivity values of the polyelectrolyte–salt system as a function of the number density of monomers in a given solvent medium and for a given salt concentration were fitted to eq 5 by the method of least-squares analysis. The best-fitted f^i values along with the standard deviations are reported in Table 3. In the representative Figures 1 to 3 we compare the calculated specific conductivities using the f^i values reported in Table 3 with those obtained experimentally. From the standard deviations recorded in Table 3, as well as from an inspection of these figures, it is directly evident that the present method of analysis reproduced the experimental results quite satisfactorily. The present experimental results, thus, provide further support in favor of the validity of the model for the conductivity of polyelectrolyte–salt solutions proposed recently by us.¹²

The present analysis also furnishes important information as to the counterion condensation behavior in polyelectrolyte–salt solutions. In any given mixed solvent medium, the fraction of uncondensed counterions decrease as the concentration of the added salt is increased indicating a suppression of the dissociation of the counterions with increasing salt concentration (cf. Table 3). An increase in the amount of acetonitrile in the acetonitrile (1) + water (2) mixtures has also been shown to cause a decrease in the fraction of uncondensed counterions. This is quite expected since the addition of acetonitrile into water causes a decrease in the relative permittivity of the medium which brings about the weakening of the counterion dissociation along the polyion backbone.

The results reported in Table 3 demonstrate that a preponderant proportion of the counterions remain condensed onto the polyion chains in the present system, the fraction of the uncondensed counterions being approximately (8 to 15) %. A survey of the literature indicated that, although studies on the

Table 3. Fractions of Uncondensed Counterions (f) and the Standard Deviations (σ) of Fit for Sodium Carboxymethylcellulose in the Presence of NaCl at 308.15 K in Acetonitrile (1) + Water (2) Mixed Solvent Media as Obtained According to eq 5

| volume fraction (v_1) | c_{NaCl} | | f | $\sigma \cdot 10^6$ |
|---------------------------|---------------------|--|-------|---------------------|
| | mol·m ⁻³ | | | |
| 0.10 | 0.1 | | 0.147 | 4.56 |
| | 1.0 | | 0.139 | 8.64 |
| | 10.0 | | 0.112 | 6.92 |
| 0.20 | 0.1 | | 0.141 | 4.53 |
| | 1.0 | | 0.133 | 7.18 |
| | 10.0 | | 0.110 | 3.73 |
| 0.40 | 0.1 | | 0.111 | 2.14 |
| | 1.0 | | 0.105 | 5.05 |
| | 10.0 | | 0.084 | 4.30 |

electrical conductances for different aqueous polyelectrolyte–salt solutions are available,^{6–10,19} in most of the cases the quantification of counterion condensation was either not attempted^{7–10} or was based^{6,19} on the Manning counterion condensation model which has subsequently been shown to be inappropriate to describe the polyelectrolyte conductivity.²⁰

Bordi et al.¹¹ reported the fractions of uncondensed counterions for aqueous sodium polyacrylate solutions to be within 0.20 to 0.25 within the polyelectrolyte concentration range (0.1 to 1.0) · 10²⁵ momomer · m⁻³ when the concentration ratio of polyelectrolyte to salt (both in equivalents per liter) was either 0.1 or 1.0. It should, however, be pointed out that a quantitative description of the experimentally determined conductivity values was not achieved in accordance with this approach.

Data on the fractions of uncondensed counterions for polyelectrolyte in the presence of a salt in mixed solvent media are not available in the literature except those reported from our laboratory where the fractions of uncondensed counterions for sodium polystyrenesulfonate in 2-ethoxyethanol + water mixtures were found to be in the range 0.19 to 0.40 for polyelectrolyte concentrations up to around 0.10 equivalents per liter in the presence of sodium chloride (0.0001 to 0.01 M).¹² The higher level of counterion condensation for sodium carboxymethylcellulose–sodium chloride in acetonitrile–water mixed solvent media demonstrates greater polyion–counterion interaction in the present media.

Studies in our laboratory are in progress to investigate how counterion condensation is influenced by the molecular weight of the polyelectrolyte species in a polyelectrolyte–salt solution. It is noteworthy that the dependence of f' on the polyelectrolyte molecular weight in salt-free solutions has already been reported in the literature.²¹ The polydispersity of the polyelectrolyte species might also, therefore, influence the f' values in polyelectrolyte–salt solutions.

CONCLUSIONS

The electrical conductances of the solutions of sodium carboxymethylcellulose in acetonitrile (1) + water (2) mixed solvent media containing (0.10, 0.20, and 0.40) volume fractions of acetonitrile (v_1) have been reported at 308.15 K in the presence of sodium chloride. The conductance data have been

analyzed on the basis of a simple equation with only one adjustable parameter developed recently by us¹² following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby et al.² using the scaling description for the configuration of a polyion chain according to Dobrynin et al.³ Excellent agreement between the experimental results and those obtained using eq 5 has always been observed. The present experimental results, thus, provide a further support in favor of the validity of the model for the conductivity of polyelectrolyte–salt solutions proposed recently by us.¹² Analyses of the results obtained also provided important information as to the influence of the medium and the salt concentration on the counterion condensation behavior of the polyelectrolyte.

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