

Electrical Conductivity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media: Experiment and Data Analysis Using the Manning Counterion Condensation Model and the Scaling Theory Approach

Introduction

Polyelectrolytes are polymers with ionizable groups which in polar solvent media dissociate into a polyion and counterions of opposite charge.¹⁻³

The description of different electrical properties of polyelectrolytes in solutions is generally based on the Manning counterion condensation theory.⁴⁻⁹ Within this model, the polyion 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 polyion and their interactions with the charged polyions are purely coulombic, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye-Hückel approximation. The solvent is assumed to be a dielectric continuum characterized by a spatially uniform relative permittivity ε . Interactions among polyions are neglected, the theory being addressed to highly diluted solutions.

Generally, the equivalent conductivity of polyelectrolyte solutions is given by⁴

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (1)$$

where 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 fraction of uncondensed counterions.

According to the Manning counterion condensation theory, polyelectrolytes have been characterized by a linear charge density parameter defined by^{4,7,9}

$$\xi = e^2 / \varepsilon k_B T b \quad (2)$$

where e is the protonic charge, ε the relative permittivity of the medium, k_B the Boltzmann constant and T the absolute temperature and b is the contour distance per unit charge. This theory states that if $\xi > 1$, enough counterions condense on to the polyion chain to yield the

critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value.

Considering the electrophoretic and relaxation contributions to the equivalent conductivity, λ_p , Manning⁴ theoretically derived the equivalent conductivity of a polyion with counterions each bearing a charge of z_c

$$\lambda_p = 279A|z_c|^{-1}|\ln \kappa a|/[1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|] \quad (3)$$

where a is the radius of the cylindrical polymer backbone, while

$$A = \varepsilon k_B T / 3\pi\eta_0 e \quad (4)$$

with η_0 being the coefficient of viscosity of the solvent. In Eq. (3), κ is the Debye screening constant, which is defined by

$$\kappa^2 = (4\pi e^2 \xi^{-1} c |z_c|) / (\varepsilon k_B T) \quad (5)$$

where c is the stoichiometric equivalent polyion concentration.

Within this model, the equivalent conductivity (Λ) is given by Eq. (1) in conjunction with Eq. (3) with f being defined as

$$f = 0.866 / \xi \quad (6)$$

Since the Manning theory applies, as stated above, to highly diluted systems where polyion-polyion interactions are assumed to be absent and to polyions modeled as a linear array of point charges, its validity is limited to very low concentration regimes of polyelectrolyte solutions.

A survey of the literature indicated that although in a limited concentration range, the change of the equivalent conductance qualitatively seems to follow the predictions of the Manning limiting law, the experimental equivalent conductance values do not generally agree with the predictions. This aspect has been amply described in the reviews by Wandrey and Hunkeler¹⁰ and Bordi *et. al.*¹¹ and no attempt is, therefore, made here to provide a comprehensive review of the vast literature that exists on this subject. However, some of the important results are given here. The article in which Manning presented⁴ the complete theoretical equation for the equivalent conductance of a salt-free polyelectrolyte solution in the limit of zero concentration was published in 1975. Interestingly, the two subsequent

articles by Kwak and Hayes¹² and Szymczak *et. al.*¹³ in that issue of the journal pointed out the discrepancies of this theory to describe satisfactorily the observed conductivity behaviour at finite concentrations. Kwak and Hayes¹² studied the electrical conductances of lithium, sodium, potassium, cesium, magnesium, calcium, and strontium salts of polystyrenesulfonic acid covering the dilute and semidilute regimes (*i.e.*, above and below the overlap concentration, c^*) at 298.15 K. They observed a minimum in the equivalent conductivity in the range 7×10^{-3} to 1×10^{-2} equiv L⁻¹ for all counterions and the two investigated polyelectrolytes of molar masses of 70000 and 500000. Whereas the initial decrease in the equivalent conductivity with increasing concentration is in agreement, at least qualitatively, with the condensation theory, the increase after the minimum was passed could not be explained. It was concluded that the applicability of the Manning theory is questionable for a concentration range where chain coiling is probable. Similar studies on the electrical conductivities on aqueous solutions of lithium, sodium, potassium, rubidium, cesium, and ammonium salts of polystyrenesulfonate in semidilute solutions were carried out by Szymczak *et. al.* at 298.15 K.¹³ Positive deviations from the limiting law are evident even at the lowest concentrations employed. They concluded that the Manning theory for electrical transport properties might require additional theoretical considerations.

Other studies of Kwak *et. al.*^{14, 15} dealt with alkali metal salts of a number of ionic polysaccharides (carboxymethylcellulose, polypectate, dextran sulfate). These authors concluded from the comparison of the various polyions carrying different charge density parameters that, although qualitative agreement is obtained with the Manning limiting law, the concentration dependence predicted is in agreement with the experimental curves only for the polyions with a relatively low charge density. The behaviour of dextran sulfate did not meet all the theoretical predictions. This was explained by the deviation from the rodlike structure on which the theory is based.

Significant deviations of the experimental equivalent conductivities of sodium and potassium dextran sulfate from the Manning predictions in the semidilute concentration regime were also reported by Beyer and Nordmeier.¹⁶

The concentration dependence of the conductivity data of tetra-*n*-alkylammonium salts of pectic acid in aqueous solutions above and below the overlap concentration also manifested large deviation from the Manning limiting law.¹⁷

Wandrey *et al.*¹⁸ made extensive use of the Manning model for conductivity of dilute and semidilute polyelectrolyte solutions in inert atmospheres and noted deviations from the model predictions.

Bordi *et al.*¹⁹ compared the predictions of the Manning model with their measured equivalent conductances obtained for poly(L-lysine) samples with molecular weights of 4000, 167000 for both the dilute and semidilute regimes. Despite the observed dependence of the equivalent conductances, the polyion conductivity is predicted to be independent of the polymer molecular weight. The prediction does not agree with either data set. The fact that the Manning model fails for the higher molecular weight sample is hardly surprising, since these data are all above c^* , while the Manning model assumes dilute solution. However, the failure of the Manning model for the lower molecular weight sample is noteworthy since these data are all below c^* .

In a study on the electrical conductivity of lithium, sodium and potassium salts of poly[(maleic acid)-co-(vinyl pyrrolidone)], Rios²⁰ confined the attention below the overlap concentration. Whereas the Manning model predicts a slow but monotonous increase in the equivalent conductivity with decreasing polyelectrolyte concentration, a maximum was observed experimentally in each of these three cases. Although, the agreement between the experiment and theory is generally poor, theoretical curves approach the experimental ones for the lithium and sodium salts over a very narrow concentration range for very dilute solutions.

It is thus apparent that the Manning limiting law for the polyelectrolyte conductivity is inappropriate because of the various unrealistic assumptions of this theory.

A new model for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt has been later proposed by Colby *et al.*²¹ using the scaling description proposed by Dobrynin *et al.*²² for the configuration of a polyelectrolyte chain.

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 $Q_p = N_\xi q_\xi = zefg N_\xi$. Due to 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 hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Following this model, in absence of added salt, the equivalent conductivity of a polyeion in a semidilute solution is given by

$$\lambda_p = (Fzefc\xi_0^2 / 3\pi\eta_0) \ln(\xi_0 / \xi_e) \quad (7)$$

where F is the Faraday number and the other symbols have their usual significance.

Thus according to this model the equivalent conductivity of a polyelectrolyte solution is given by Eq. (1) with the λ_p value obtained from Eq. (7).

Within this model, the parameter f - that defines the fraction of uncondensed counterions in the Manning sense - has been treated as an adjustable one. Whereas the Manning theory applies to polyelectrolyte solutions in the highly diluted regime and predicts a fraction of condensed counterions independent of the polymer concentration, the Colby model can be applied to more concentrated systems, up to the concentration c_D , where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size. This new model has been applied, so far, to a limited number of aqueous polyelectrolytes^{11, 19, 21} and good agreement with the experiment was observed. Moreover, this model has been successfully employed to identify concentration regimes differing in the fractions of uncondensed counterions.²³ This model, however, has not been applied to polyelectrolyte solutions in solvents besides water.

Although studies on the polyelectrolyte conductivity in salt-free aqueous solutions are now plentiful at 298.15 K,^{10, 11} not much attention was paid to such studies dealing with temperature dependence.^{16, 17, 19, 24, 25} The situation worsens in mixed solvent media. Only a few investigations has so far been made²⁶⁻²⁸ at a given temperature. To our knowledge, there has been no attempt to study the conductivity behaviour of salt-free polyelectrolyte solutions in mixed solvent as a function of temperature except those reported from our laboratory.²⁹⁻³¹ In our earlier investigations on polyelectrolyte conductivity in mixed solvent media, we have demonstrated the failure of the Manning model for these systems. Here we present a study on the electrical conductivity of the semidilute solutions of sodium polystyrenesulfonate in

acetonitrile-water mixed solvent media at different temperatures. We have also observed inapplicability of the Manning model here and have therefore analysed the data on the basis of the scaling theory. This is, in fact, the first report on the application of the scaling theory approach to semidilute polyelectrolyte conductivity in mixed solvent media. The influences of concentration, medium, and temperature on the extent of uncondensed counterions as well as on the mobility of the polyelectrolyte species have also been investigated.

Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. Triply distilled water with a specific conductance of less than 10^{-6} S cm⁻¹ at 308.15 K was used for the preparation of the solvent mixtures. The physical properties of acetonitrile-water mixtures used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1 of Chapter III.

Also included in this table are the limiting equivalent conductivity of the counterion (Na⁺), λ_c^0 , in 20 and 40 volume percent of acetonitrile-water mixtures which were reported earlier³² (*cf.* Appendix).

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 70 kDa.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz with negligible polarization effects using a dip-type cell with a cell constant of 1.15 cm⁻¹ and having an uncertainty of 0.01%. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier.³³ Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium (κ_0) from those of the polyelectrolyte solutions (κ).

In order to avoid moisture pickup, the experimental solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates and the results were averaged.

Results and Discussion

Experimental Equivalent Conductivity

The experimental equivalent conductivities (Λ) for sodium polystyrenesulfonate as a function of the square root of the polyelectrolyte concentration (\sqrt{c}) in two acetonitrile-water mixed solvent media (containing 20 and 40 vol% of acetonitrile) at 308.15, 313.15, and 318.15 K over the entire concentration range investigated are shown in Figures 1 and 2. From these figures, it is evident that the present species demonstrates typical polyelectrolyte behavior in which the equivalent conductivities exhibit a slight increase with decreasing concentration. Equivalent conductivities of sodium polystyrenesulfonate have been reported earlier in pure water as a function of polyelectrolyte concentration and temperature.²⁴ Davydova *et. al.*²⁵ reported the temperature dependence of the mean charge spacing (b) for of aqueous sodium polystyrenesulfonate solutions; but the experimental equivalent conductivity values were not available and hence a comparison with our results is not possible. A comparison of our results with those reported in reference²⁴ indicates that the Λ values in acetonitrile-water mixtures are always higher than the corresponding values in water. This may be ascribed to greater solvation of the sodium counterions in aqueous solution.

The effects of temperature on the equivalent conductivity values are directly evident from the Figures 1 and 2, where in a given solvent medium Λ values are found to increase with temperature over the entire concentration range. At each temperature, however, the Λ values are found to decrease with decreasing relative permittivity in going from 20 percent to 40 percent acetonitrile-water mixtures over the entire concentration range investigated as illustrated in Figures 1 and 2. This is quite expected because as the relative permittivity of the medium decreases, interaction between polyion and counterions is expected to increase with concomitant lowering in the mobilities of the conducting species and hence in that of 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 Λ values with those calculated using the Manning theory. It may be mentioned that no attempt was made earlier to correlate the experimental equivalent conductivities of sodium polystyrenesulfonate obtained at different temperatures in aqueous solutions with the Manning predictions.^{24,25} The charge density

parameters (ξ) were calculated from Eq. (2) using the literature value for the length of the monomer unit having one charged group (b)³⁴ and are reported in Table 1. The theoretical values of λ_p and hence of Λ , are dependent on a , the radius of the polyion cylinder. For the radius of the assumedly rod-like polymer cylinder, we used a value of 8 \AA^0 for the present analysis.³⁴

Graphical representation of the theoretical predictions (solid lines) based on this model along with the experimental Λ values (points) are included in Figures 1 and 2 at 308.15, 313.15, and 318.15 K in acetonitrile-water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. The same situation of negative deviation^{13, 17} as well as positive deviation^{20, 35} from the experimental values was also noticed for other polyelectrolyte solutions. The discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies Eq. (5).

Comparison with the Scaling Theory Approach

The reason for the failure of the Manning model in the present investigation can be understood if one estimates the overlap concentration (c^*) for the polymer chain investigated using the following equation

$$c^* = 1/N_{\Lambda}L^2a \quad (8)$$

where the symbols have their usual significance. It is observed that the polymer solutions used in the present study are essentially in the semidilute regime ($c > c^* \approx 0.001 \text{ eqiv L}^{-1}$) where the Manning limiting law does not apply.

We, therefore, have taken the recourse of the approach proposed by Colby *et. al.*²¹ for semidilute polyelectrolyte solutions, for the analysis of our conductivity data.

Since the present acetonitrile-water mixtures are poor solvent for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule, we use a value of 5 \AA^0 as the effective monomer size (b) as suggested by Colby *et. al.*²¹

Under poor solvent condition, the electrostatic blob size (ξ_c) and the correlation blob size (ξ_0) are given by²¹

$$\xi_e = b(A^2 / \xi)^{1/3} \quad (9)$$

$$\xi_0 = (cb)^{-1/2} (A^2 / \xi)^{1/3} \quad (10)$$

In Figures 1 and 2, the predictions of the Colby model (dashed lines) for the semidilute regime have been compared with the experimental data. The Colby model is found to reproduce the experimental results here quite satisfactorily.

The agreement of the theory with the experimental data is particularly significant considering that the theory requires only one adjustable parameter, namely the fraction of uncondensed counterions (f), to describe the experimental results. A closer look at the Figures 1 and 2 as well as the standard deviations of the fits recorded in Table 2, however, reveal that although the scaling theory approach provides a dramatic improvement over the Manning model with a constant level of counterion condensation with polyelectrolyte concentration, the usual assumption that the effective charge on a polyion chain is independent of the polymer concentration is no longer valid for the system under investigation.

The measured fraction of uncondensed counterions and its dependence on temperature and relative permittivity

Since the fractions of uncondensed counterions (f) were found to vary with the polymer concentrations, we have calculated the fractions from our conductivity data using Eq. (1) in conjunction with Eq. (7). The concentration dependence of f thus obtained is shown in Figures 3 and 4. These figures demonstrate that the fraction of the uncondensed counterions does not remain fixed over the concentration range investigated in the present study (3-5% increase in the fraction of uncondensed counterions was observed).

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 (Figures 3 and 4). Since decreasing relative permittivity should result in a greater interaction between the polyion and counterions, the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower - as has been observed in the present study.

The influence of temperature on the f value in the present mixed solvent media is, at first sight, rather perplexing. For any given mixed solvent system, the fraction of

uncondensed counterions is found to decrease with increasing temperature (Figures 3 and 4) which apparently contradicts the experimental observation in Figures 1 and 2 where the equivalent conductivity increases with temperature in each of the mixed solvent medium investigated. This can be ascribed to a change in solvation and condensation behavior of 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 due to a temperature-induced increase in the speed of the ions in a lower viscous medium at higher temperatures.

Conclusions

An investigation on electrical conductivity of salt-free solution of an anionic polyelectrolyte - sodium polystyrenesulfonate - in acetonitrile-water mixed solvent media has 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 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 could not be quantitatively described by the Manning counterion condensation theory. This discrepancy probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model valid only at infinite dilution that underlies this theory. A recent model proposed by Colby *et. al.*²¹ based on scaling considerations for the configuration of a polyelectrolyte chain in semidilute solution has also been tested and the results derived from this model are found to be quantitatively consistent with the experimental observations. A closer look, however, reveals that although the scaling theory approach on the basis of a constant level of counterion condensation provides a dramatic improvement over the Manning model, the fraction of the uncondensed counterions does not remain fixed over the concentration range investigated in the present study. The influences of temperature and the relative permittivity of the medium on the equivalent conductivity as well as the fractions of uncondensed counterions were also investigated.

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Table 1. Charge Density Parameters (ξ) Used for the Manning Counterion Condensation Theory and the f Values for the Best-fit of the Experimental Equivalent Conductances following Scaling Theory Approach for Sodium Polystyrenesulfonate in Acetonitrile-Water Mixtures Containing 20 and 40 Volume Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

Volume percent of acetonitrile	$T = 308.15$ K	$T = 313.15$ K	$T = 318.15$ K
Manning Charge Density Parameters (ξ)			
20	3.17 (52.00)	3.19 (55.01)	3.22 (59.20)
40	3.58 (40.61)	3.60 (46.43)	3.64 (50.57)
Best-fit f Values (Scaling Theory Approach)			
20	0.368 (1.88)	0.344 (2.09)	0.330 (2.52)
40	0.275 (1.11)	0.267 (1.48)	0.242 (1.70)

Standard deviations of the fits are given within the parentheses.

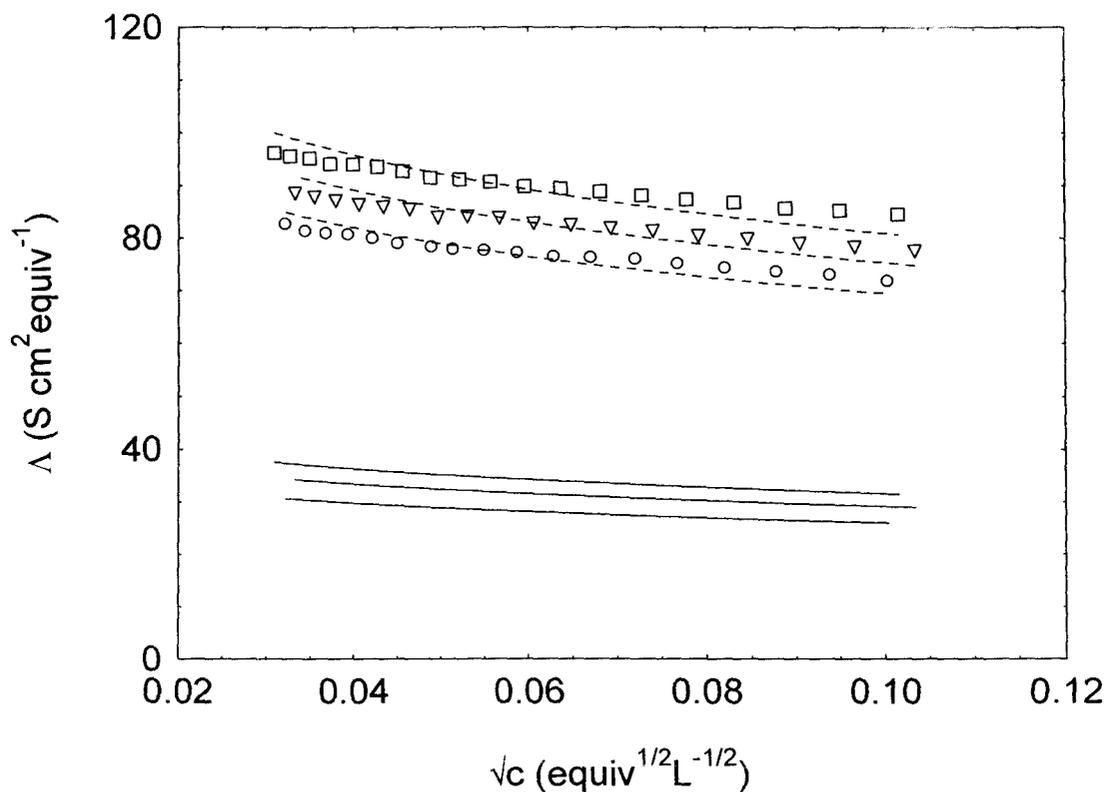


Figure 1. Comparison of the experimental values of the equivalent conductivity (Λ) as a function of the square root of the polyelectrolyte concentration (\sqrt{c}) for sodium polystyrenesulfonate in 20 vol percent of acetonitrile in acetonitrile-water mixture with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory. Experimental: 308.15 K (\circ), 313.15 K (Δ), and 318.15 K (\square). Manning theory: solid lines for 308.15, 313.15, and 318.15 K respectively from bottom to top. Scaling theory: dashed lines.

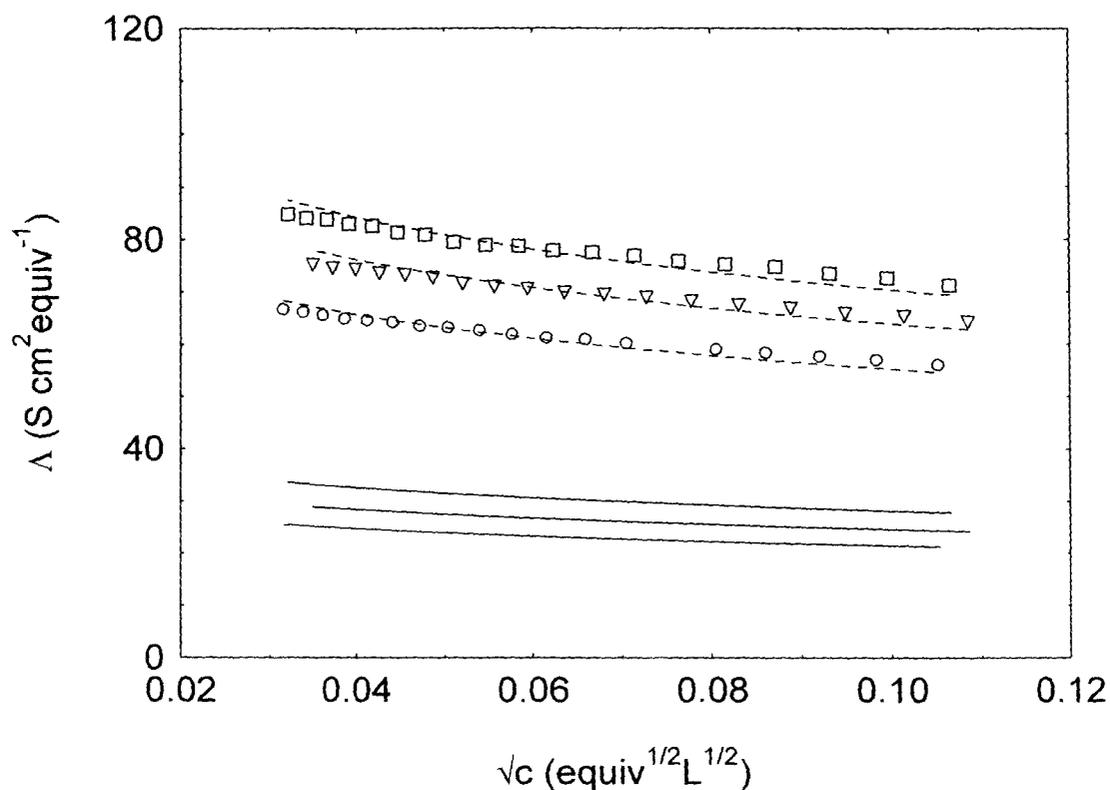


Figure 2. Comparison of the experimental values of the equivalent conductivity (Λ) as a function of the square root of the polyelectrolyte concentration (\sqrt{c}) for sodium polystyrenesulfonate in 40 vol percent of acetonitrile in acetonitrile-water mixture with those predicted on the basis of the Manning counterion condensation theory and on the basis of the scaling theory. Experimental: 308.15 K (\circ), 313.15 K (Δ), and 318.15 K (\square). Manning theory: solid lines for 308.15, 313.15, and 318.15 K respectively from bottom to top. Scaling theory: dashed lines.

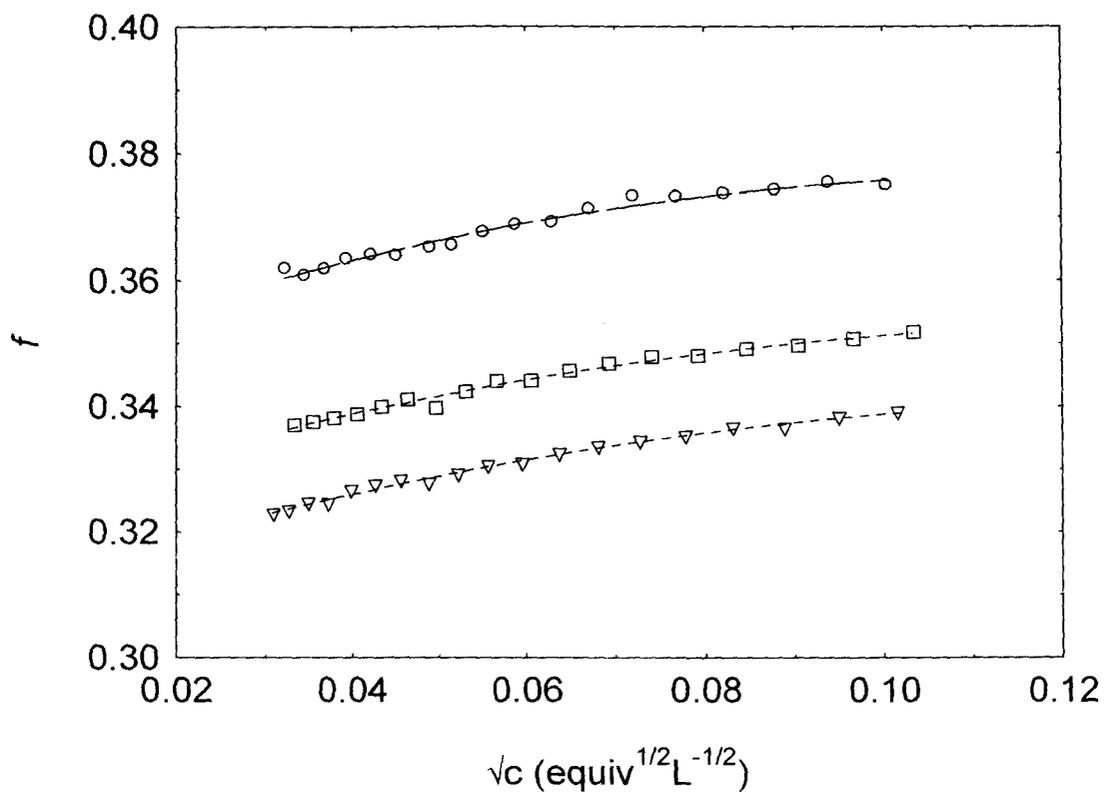


Figure 3. Fraction of uncondensed counterions (f) as a function of the square root of the polyelectrolyte concentration (\sqrt{c}) for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media containing 20 vol percent of acetonitrile, calculated using the scaling approach from the conductivity data: 308.15 K (open circles), 313.15 K (\square), and 318.15 K (open triangles). The dashed lines are used to guide the eye.

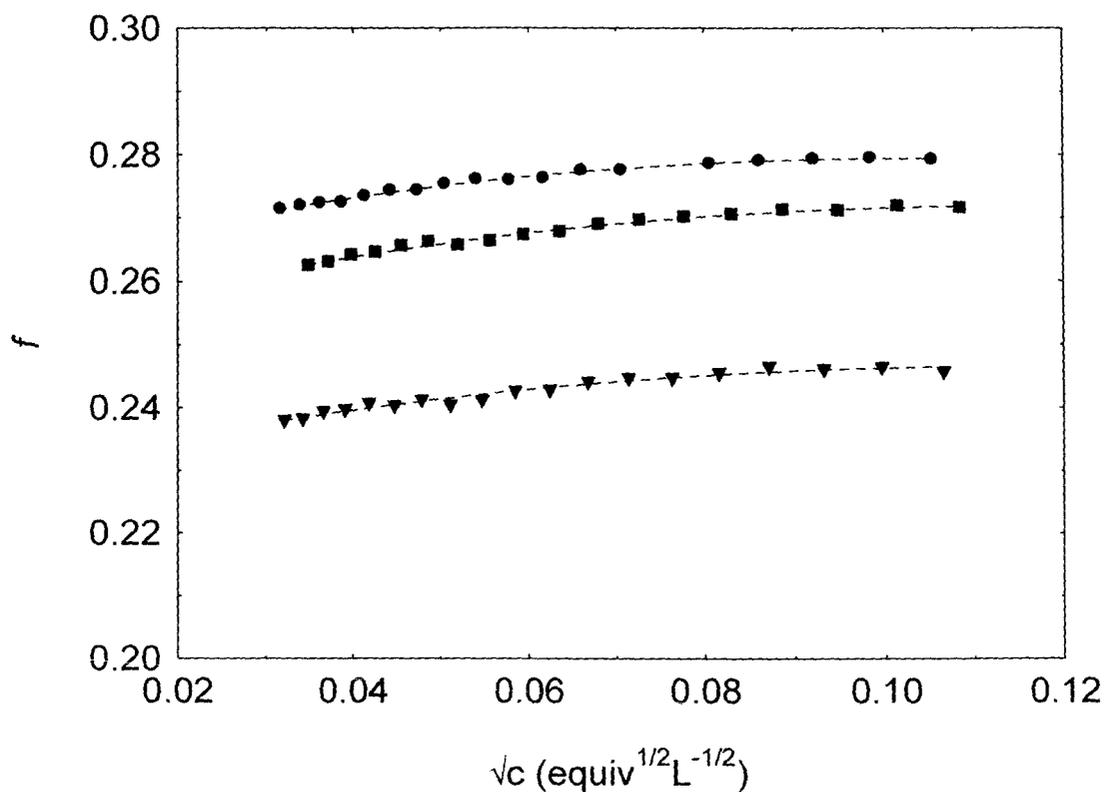


Figure 4. Fraction of uncondensed counterions (f) as a function of the square root of the polyelectrolyte concentration (\sqrt{c}) for sodium polystyrenesulfonate in acetonitrile-water mixed solvent media containing 40 vol percent of acetonitrile, calculated using the scaling approach from the conductivity data: 308.15 K (●), 313.15 K (■), and 318.15 K (▲). The dashed lines are used to guide the eye.