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Influence of temperature, added electrolyte, and polymer molecular weight on the counterion-condensation phenomenon in aqueous solution of sodium polystyrenesulfonate: A scaling theory approach

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Abstract: Interactions between a polyion and its counterions in aqueous solutions of an anionic polyelectrolyte sodium polystyrenesulfonate in presence of sodium chloride were investigated using electrical conductivity as the probe. The specific conductivity vs. polyelectrolyte concentration data were analyzed with an equation recently developed by us considering the scaling description for the conformation of a polyion chain. The influences of (a) the molecular weight and the concentration of the polyelectrolyte, (b) the added electrolyte concentration, and (c) the temperature on polyion-counterion interactions were investigated. The extent of counterion condensation was found to be greatly affected by the concentration and molecular weight of the polyelectrolyte, the concentration of the added electrolyte, and the temperature. The polyion equivalent conductivity in conjunction with the derived coefficient of friction between the monomer units and the solvent provided important information concerning the relative importance of the size and charge of the polyions. The overall results have been elucidated taking the medium dielectric constant, the hydration behaviour of the counterions, and the coiling behavior of the polyion chains into account. The present study provides new insight as to how the polyelectrolyte molecular weight influences the counterion condensation behaviour in a polyelectrolyte solution in presence of an added electrolyte.

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Introduction

Polyelectrolytes are polymers whose repeating units bear an electrolyte group which dissociate in aqueous solutions to yield a macroion or polyion and oppositely charged counterions.[1,2] The Coulombic attraction leads to a spatial correlation of the counterions with the macroion. This correlation makes the aqueous solutions of polyelectrolytes behave entirely differently from the neutral (uncharged) polymeric species, thus influencing a variety of their transport and colligative properties. The unique properties of polyelectrolytes render them a system of fundamental interest in the physics of soft-condensed matter including biomacromolecules.[1-9] They also find a variety of technological applications. In many applications as well as in biological systems both polyelectrolytes and ions derived from electrolytes coexist, where polyelectrolyte-salt interactions play a pivotal role. A quantitative elucidation of these interactions requires a thorough understanding of the condensation of counterions onto the polyion chains which would help unravel the effects of solution conditions on biological and industrial systems involving polyelectrolytes. Despite decades of research, the phenomenon of counterion condensation in polyelectrolyte solutions is not fully understood owing primarily to the intricate coupling of various interactions in these systems.[5-17] The ionic interactions between the polyion and the counterions characterizing the polyelectrolyte behavior can be conveniently investigated by measuring the electrical conductivity because it takes into account the movement of any charged entity present in aqueous solutions (polyion, counterions, and ions derived from the added salt) when an external electric field is applied.

Electrical conductivities of polyelectrolyte solutions were first considered by Manning quantitatively on the basis of counterion condensation model.[18-20] 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 dielectric constant ε. Interactions among the polyions are neglected, the theory being addressed to highly diluted solutions. The equations derived on the basis of these assumptions can, therefore, be considered as the limiting laws.

The equivalent conductivity (Λ) of a polyelectrolyte dissolved in solution is given by[20]

$$\Lambda = f(\lambda_c^0 + \lambda_\mathrm{p}) \tag{1}$$

where f is the fraction of free counterions, λ_c^0 the equivalent conductivity of the counterions at infinite dilution, and λ_p the equivalent conductivity of the polyion at any given concentration.

In the frame of the Manning counterion condensation model, a polyelectrolyte is characterized by the charge parameter (ξ) which is defined through the ratio of the Bjerrum length (λ_B) to the distance between two adjacent charged groups on the polyion (b):

$$\xi = \frac{\lambda_\mathrm{B}}{b} \tag{2}$$

with λ_B being defined by

$$\lambda_\mathrm{B} = \frac{e^2}{\varepsilon k_\mathrm{B} T} \tag{3}$$

where e is the charge of an electron, ε the dielectric constant of the solvent medium, k_B the Boltzmann constant and T the temperature in absolute scale. According to this model, if $\xi > 1$, enough counterion condensation on to the polyion chain commences till the critical value $\xi = 1$ is reached. If, on the other hand, $\xi < 1$, dissociation of counterions takes place to reach the critical value of the charge parameter. The fraction of free counterions (f) is, according to Manning,[20] given by

$$f = \frac{0.866}{\xi} \tag{4}$$

Manning[20] derived the following expression for the equivalent conductivity of a polyion along with counterions each with a charge of z_c taking into account the electrophoretic and relaxation effects

$$\lambda_\mathrm{p} = \frac{279A\left|z_\mathrm{c}\right|^{-1}\left|\ln\left(r_\mathrm{D}^{-1}a\right)\right|}{1 + 43.2A\left(\left|z_\mathrm{c}\right|\lambda_\mathrm{c}^0\right)^{-1}\left|\ln\left(r_\mathrm{D}^{-1}a\right)\right|} \tag{5}$$

where a is the radius of the polyion cylinder, while

$$A = \frac{\varepsilon k_B T}{3\pi\eta e} \tag{6}$$

with η being the bulk viscosity and κ the Debye screening length defined by

$$r_\mathrm{D} = \left(\frac{4\pi N_\mathrm{A} e^2 \xi^{-1} c\left|z_\mathrm{c}\right|}{\varepsilon k_\mathrm{B} T}\right)^{-1/2} \tag{7}$$

with c being the stoichiometric equivalent polyion concentration (in moles of monovalent charged groups in unit volume).

Therefore, the equivalent conductivity of a polyelectrolyte solution (Λ) can, according to Manning,[20] be expressed as

$$\Lambda = \frac{0.866}{\xi}\left[\lambda_\mathrm{c}^0 + \frac{279A\left|z_\mathrm{c}\right|^{-1}\left|\ln\left(r_\mathrm{D}^{-1}a\right)\right|}{1 + 43.2A\left(\left|z_\mathrm{c}\right|\lambda_\mathrm{c}^0\right)^{-1}\left|\ln\left(r_\mathrm{D}^{-1}a\right)\right|}\right] \tag{8}$$

The specific conductivity of the polyelectrolyte solution in presence of an added electrolyte (σ) will be given by[33,34]

$$\sigma = \sigma_{\mathrm{s}} + \frac{0.866}{\xi} c \left[\lambda_{\mathrm{c}}^{0} + \frac{279 A \left| z_{\mathrm{c}} \right|^{-1} \left| \ln \left(r_{\mathrm{D}}^{-1} a \right) \right|}{1 + 43.2 A \left(\left| z_{\mathrm{c}} \right| \lambda_{\mathrm{c}}^{0} \right)^{-1} \left| \ln \left(r_{\mathrm{D}}^{-1} a \right) \right|} \right] \tag{9}$$

where σ_{s} is the specific conductivity of the salt solution in absence of the polyelectrolyte.

It should be pointed out that the Manning theory is, in principle, applicable to polyelectrolyte solutions as the polyelectrolyte concentration approaches zero characterizing the absence of polyion-polyion interactions where polyions can be modeled as a rigid linear array of point charges. Hence, the quantitative conclusions drawn from this theory cannot be compared with the experimental data measured at finite concentrations especially in the semidilute regime where the interpolyionic interactions cannot be neglected. Flexible polyelectrolytes cannot also be treated with this model since the conformation of the polyion chains in these cases varies with their concentration as opposed to the underlying assumption of this model.[21-26]

Later, Colby *et al*[27] developed a simple model of AC conductivity for salt-free semidilute polyelectrolyte solutions using the de Gennes scaling picture for the configuration of a polyelectrolyte chain in semidilute solution according to Dobrynin *et al*.[28] This model considered the concentration dependence of polyion chain flexibility and the mutual interactions among the polyion chains which were not taken into account in the Manning counterion condensation theory. This approach has been found to be successful to describe the conductivity of semidilute polyelectrolyte solutions.[27, 29-32]

In a semidilute polyelectrolyte solution, Colby *et al*,[27] considered a polyion chain as an assembly of randomly walking N_{ξ} correlation blobs each with a size of ξ_0. Each correlation blob contains g monomers and bears an electric charge of $q_{\xi} = \left| z_{\mathrm{c}} \right| efg$. The entire chain with a contour length of $N_\xi \xi_0$, carries a charge of $|z_\mathrm{c}|efgN_\xi$. The strong electrostatic interactions within the correlation blobs cause the chain to attain a completely extended conformation of g_e electrostatic blobs each of size D.

Within this model, Colby *et al.*,[27] arrived at the following expression of the equivalent conductivity of a salt-free solution of a polyion (λ_p)

$$\lambda_\mathrm{p} = \frac{F|z_\mathrm{c}|efg\ln(\xi_0/D)}{3\pi\eta\xi_0} \tag{10}$$

where F is the Faraday constant.

The equivalent conductivity of a the polyelectrolyte solution is, therefore, given by

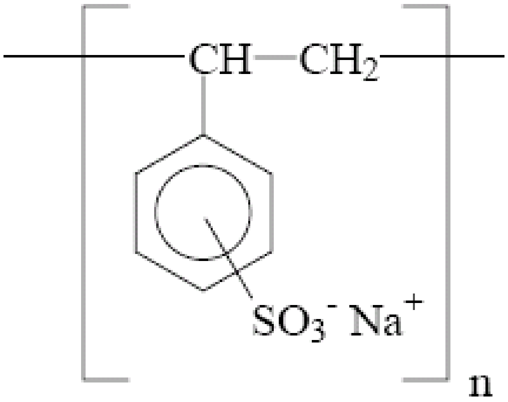
$$\Lambda = f\left[\lambda_\mathrm{c}^0 + \frac{F|z_\mathrm{c}|efg\ln(\xi_0/D)}{3\pi\eta\xi_0}\right] \tag{11}$$

The specific conductivity of a polyelectrolyte solution in presence of an added electrolyte will be given by

$$\sigma = \sigma_\mathrm{s} + fc\left[\lambda_\mathrm{c}^0 + \frac{F|z_\mathrm{c}|efg\ln(\xi_0/D)}{3\pi\eta\xi_0}\right] \tag{12}$$

The above equation has only one adjustable parameter, namely the fraction of free counterions. This parameter can be ascertained by least-squares fit of the measured specific conductivity of the polyelectrolyte-salt solution (σ) to Eq. (12) in conjunction with the experimental specific conductance (σ_S) of the polyelectrolyte-free salt solution. The value of *f* appearing in the above equation takes care of the modified polyion-counterion interactions upon addition of the salt to the polyelectrolyte solution.

This equation has been successfully employed to describe quantitatively the electrical conductivities of polyelectrolyte-salt solutions,[33-35] and hence would help unravel the interactions



Scheme 1 Chemical structure of NaPSS.

characterizing the polyelectrolyte-salt solutions, in general, and the biopolymer-salt solutions (*e.g.*, protein-salt, DNA-salt solutions etc.), in particular.

Thus, it is intended in this study to investigate the counterion condensation behavior of aqueous sodium polystyrenesulfonate (NaPSS) solutions in presence of an added electrolyte considering a multitude of parameters including polymer molecular weight, polyelectrolyte concentration, added salt concentration and the temperature. The present study reported for the first time the effect of polymer molecular weight on the counterion condensation phenomena in polyelectrolyte-salt solutions and clearly demonstrated the significance of the polyion chain conformation on the polyion mobility.

Experimental section

Materials. Two NaPSS samples with average molecular weights of 70000 and 1000000 each with a degree of substitution of one employed in this investigation was purchased from Aldrich Chemical Company, Inc. The chemical structure of the NaPSS sample used in this study is depicted in Scheme 1. The average molecular weights of the samples were estimated from the intrinsic viscosity value determined in presence of 0.05 mol L^{-1} NaCl aqueous solution at 298.15

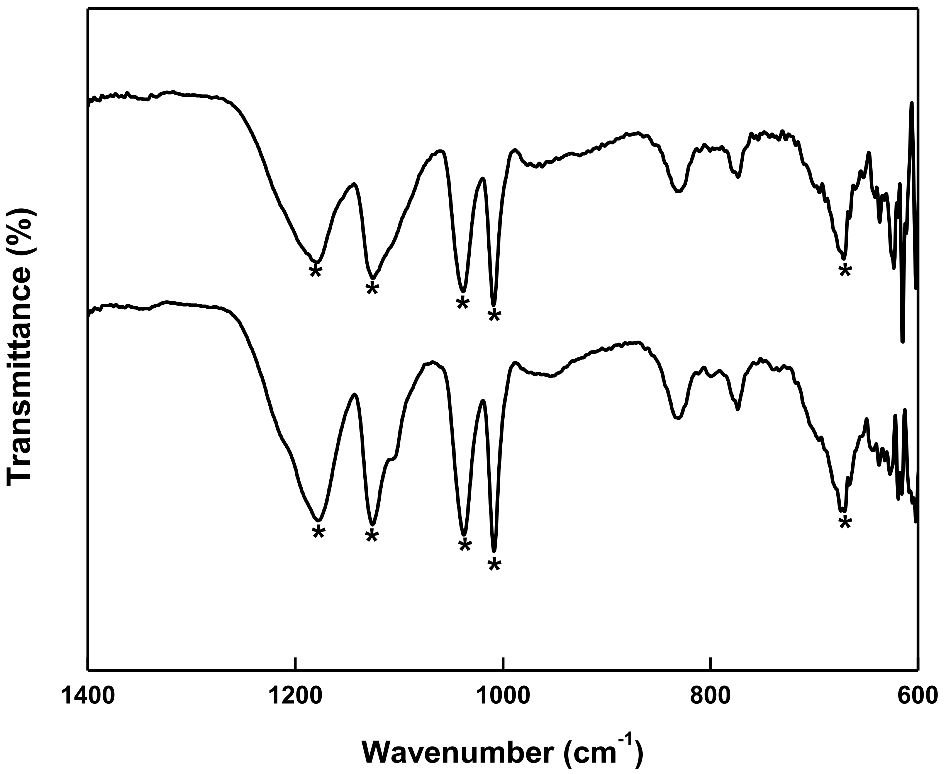


Fig. 1 FT-IR spectra NaPSS samples: Molecular weight 70000 (top spectrum) and 1000000 (bottom spectrum).

K using the Mark-Houwink equation with the constants obtained from the literature.[36] The molecular weights reported by the manufacturer agreed well with those determined in the present study. The Fourier Transform Infrared Spectra (FT-IR) of both polymer samples are shown Fig. 1 with characteristic peaks indicated by * symbol. The characteristic peaks were observed at about 1182, 1128, 1040, 1010 and 669 cm^{-1}. These characteristic peaks agree very well with those reported earlier for NaPSS samples.[37,38] The SO_3^- group antisymmetric and symmetric vibrational adsorption peaks can be assigned to the peaks at 1182 and 1038 cm^{-1}, respectively.[38] Peaks at 1130 and 1011 cm^{-1} can be assigned to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring.[38] Incomplete sulfonation of NaPSS would show peaks at around 699 and 758 cm^{-1}; absence of such peaks in the FT-IR spectra confirms the manufacturer's report that the studied NaPSS samples are fully sulfonated.

NaCl was purchased from Fluka (puriss grade) and was dried *in vacuo* for a prolonged period immediately prior to use.

Triply distilled water having a specific conductivity of *ca*. 10^{-6} S cm^{-1} at 308.15 K was employed for the preparation of the solutions.

Conductivity measurements. An Orion (Thermo Fisher, USA) conductivity meter was used to measure the specific conductivities taking solutions in a wide mouth test tube fitted with a dip-type cell (cell constant = 1 cm^{-1}). The uncertainty of measurements was 0.01%. The conductivity measurements were performed in a water thermostat maintained within ± 0.01 K of the experimental temperature. Calibration of the cell was done with potassium chloride (aq) solutions by using the method of Lind *et al*.[39] The specific conductivities of the solutions (σ) were always solvent corrected. Each experiment was performed in 3-5 replicates and their average values were used for calculation.

Viscosity measurements. A suspended level Ubbelohde viscosimeter was used for measuring the viscosities of the experimental solutions. The viscosimeter was kept vertically in a water thermostat maintained within ±0.01 K of the desired temperature. The absolute viscosity (η) can then be obtained from:

$$\eta = \left(Ct - \frac{K}{t} \right) \rho \tag{13}$$

where t is the time of flow, ρ is the density of the experimental liquid, and C and K are two constants characteristic of the viscosimeter. The values of C and K were determined by using the

Table 1 Physical properties of water and the limiting ionic equivalent conductivities of sodium ion in water at 298.15, 308.15, and 318.15 K

Temperature (K)	η (P)	ε	λ_c^0 (S cm^2 eqv^{-1})
298.15	0.008903	78.30	50.10
308.15	0.007194	74.82	61.54
318.15	0.005963	71.51	73.73

known literature density and the viscosity data of water, and 2-methoxyethanol.[40] These values of C and K were estimated to be 1.646×10^{-5} cm^2 s^{-2} and -0.02331647 cm^2, respectively. These were further checked with methanol and acetonitrile.[41, 42]

Fourier transform-infrared (FTIR) spectral measurements. FT-IR spectra of NaPSS samples were acquired by attenuated total reflectance (ATR) technique using a Jasco FTIR-4200 spectrometer with a frequency resolution of 2 cm^{-1}.

Results and discussion

Solvent properties and the limiting equivalent conductivity of Na$^+$ ion. Table 1 reports the measured coefficients of viscosity (η) and the literature[43] dielectric constants (ε) of water at the experimental temperatures. The values of the equivalent conductivities of the counterion (Na$^+$) at infinite dilution in water (λ_c^0) were taken from the literature[43] and are also included in this table.

Experimental specific conductivities. A representative plot (Fig. 2) shows the variation of the experimental specific conductivities (σ) of aqueous solutions of NaPSS as a function of the square root of the moles of monomers of the polyelectrolyte sample per cm^3 (c_p) with varying

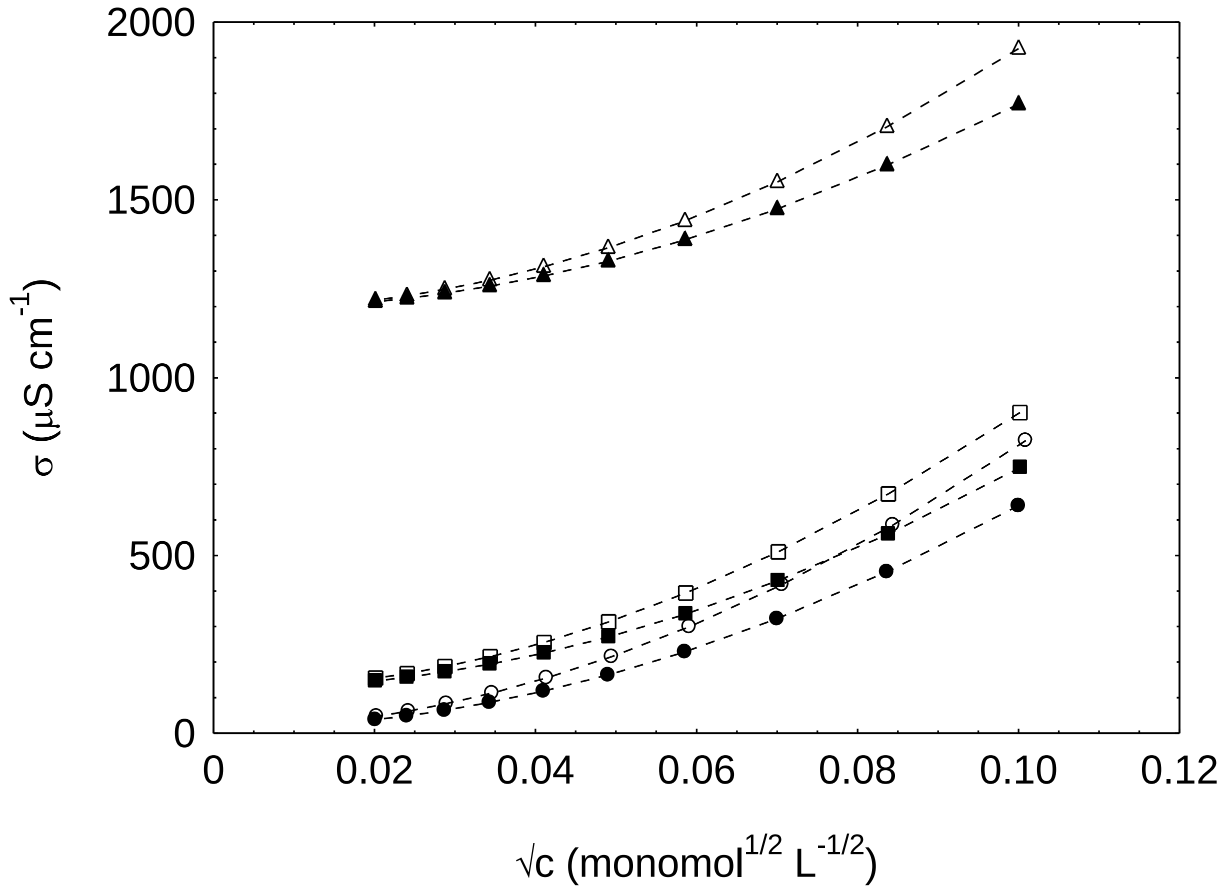


Fig. 2 Experimental specific conductivities (κ) of NaPSS in the presence of varying concentrations of NaCl [0.0001 (circles), 0.0010 (squares), and 0.0100 (triangles) mol L^{-1}] in water as a function of the square root of the polyelectrolyte concentration at 298.15 K. The open symbols refer to the NaPSS sample with a molecular weight of 70000 whereas the closed symbols to the NaPSS sample with a molecular weight of 1000000.

concentrations of the added salt NaCl (0.0001, 0.0010, and 0.0100 mol L^{-1}) for two different molecular weights of the polyelectrolyte, namely 70000 and 1000000 at 298.15 K. The corresponding figures at 308.15 and 318.15 K are available as Supplementary material (Figs. 1S and 2S). The specific conductivities are, in all cases, found to be increased with polyelectrolyte concentration. Addition of salt caused an increase in the specific conductivities of the polyelectrolyte solutions as expected.

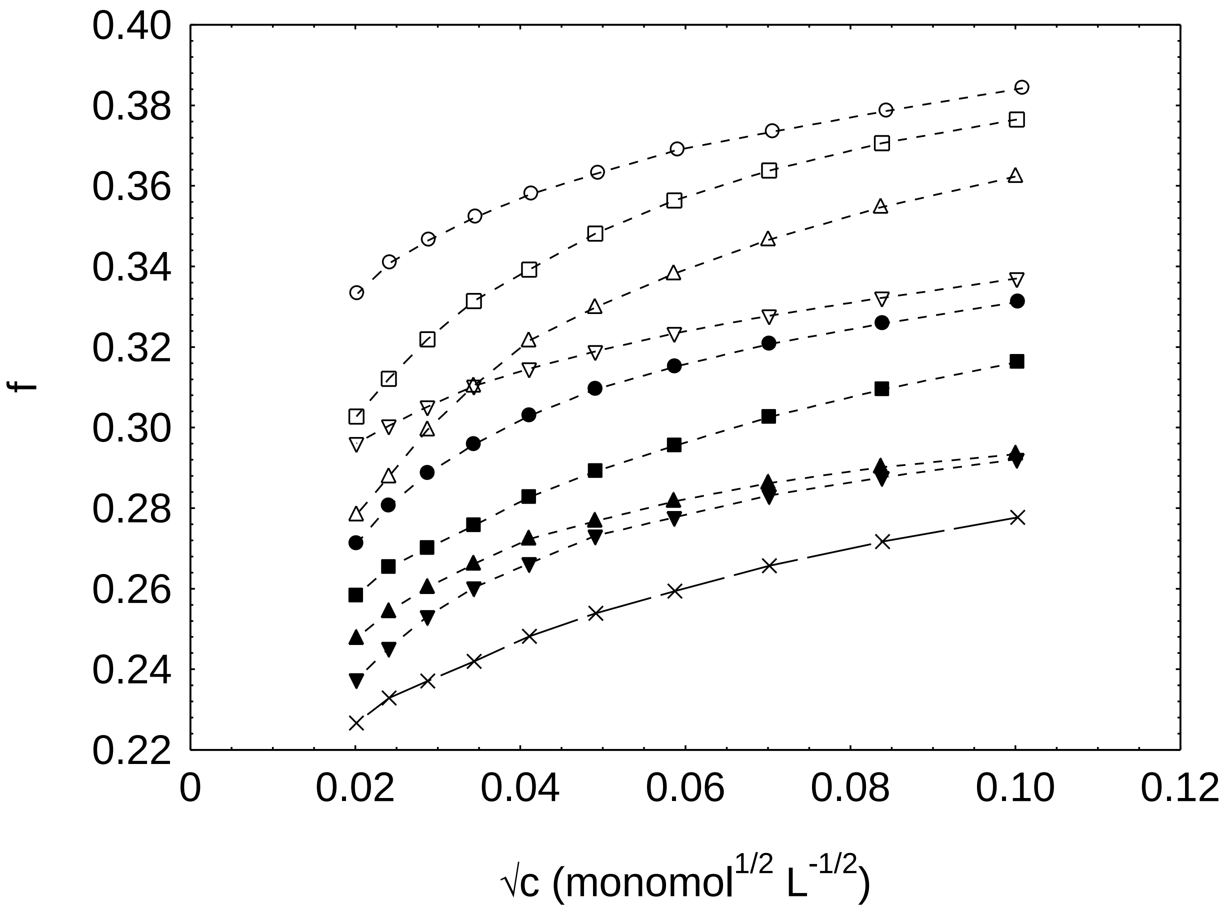


Fig. 3(a) Fraction of free counterions in aqueous solution of NaPSS (molecular weight = 70000) in presence of NaCl at different temperatures. Significance of symbols - open circles: 0.0001 M NaCl at 298.15 K; open squares: 0.001 M NaCl at 298.15 K; open up triangles: 0.01 M NaCl at 298.15 K; open down triangles: 0.0001 M NaCl at 308.15 K; filled circles: : 0.001 M NaCl at 308.15 K; filled squares: 0.01 M NaCl at 308.15 K; filled up triangles: 0.0001 M NaCl at 318.15 K; filled down triangles: 0.001 M NaCl at 318.15 K; crosses: 0.01 M NaCl at 318.15 K.

Fraction of free counterions. The present specific conductivity data have been analyzed on the basis of Eq. (9). Two key size parameters, namely the sizes of the electrostatic blob (D) and that of the correlation blob (ξ_0) appearing in Eq. (9) depend upon the quality of the solvent. For poor solvents, these are given by[27]

$$D = b\left(\xi f'^{2}\right)^{-1/3} \tag{14}$$

$$\xi_0 = (c'b)^{-1/2}\left(\xi f'^{2}\right)^{-1/3} \tag{15}$$

where c' is the number density of monomers. For good solvents, on the other hand, these are given by[27]

$$D = b\left(\xi f'^{2}\right)^{-3/7} \tag{16}$$

$$\xi_0 = (c'b)^{-1/2}\left(\xi f'^{2}\right)^{-1/7} \tag{17}$$

As pointed out by Colby *et al.*,[27] we used the poor solvent correlations for the analysis of the present experimental data on aqueous NaPSS solutions.

The scaling theory approach, with only one adjustable parameter *f* over the entire concentration range provided a very good description of the experimental specific conductivity vs. concentration data for polyelectrolyte solutions in presence of an added salt due mainly to the fact that this approach takes into account the concentration-dependent conformational change of the polyions, and the interactions between them in these solutions. A quantitative description of the experimental results could, however, not be achieved in some cases.[33] It can thus be inferred that the assumption of the independence of the effective charge on a polyion chain of the polymer concentration is no longer valid for the system under investigation. Keeping this in view, in the present investigation, we have calculated the fractions of free counterions (*f*) independently at each polyelectrolyte concentration with Eqs. (9), (14) and (15). The values of *f* are found to vary significantly with NaPSS concentration. This observation suggests that the effective charge on the polystyrenesulfonate chains is dependent on NaPSS concentration.

The results obtained will now be discussed to extract useful information concerning the influence of added salt on the counterion condensation behavior in polyelectrolyte solutions with

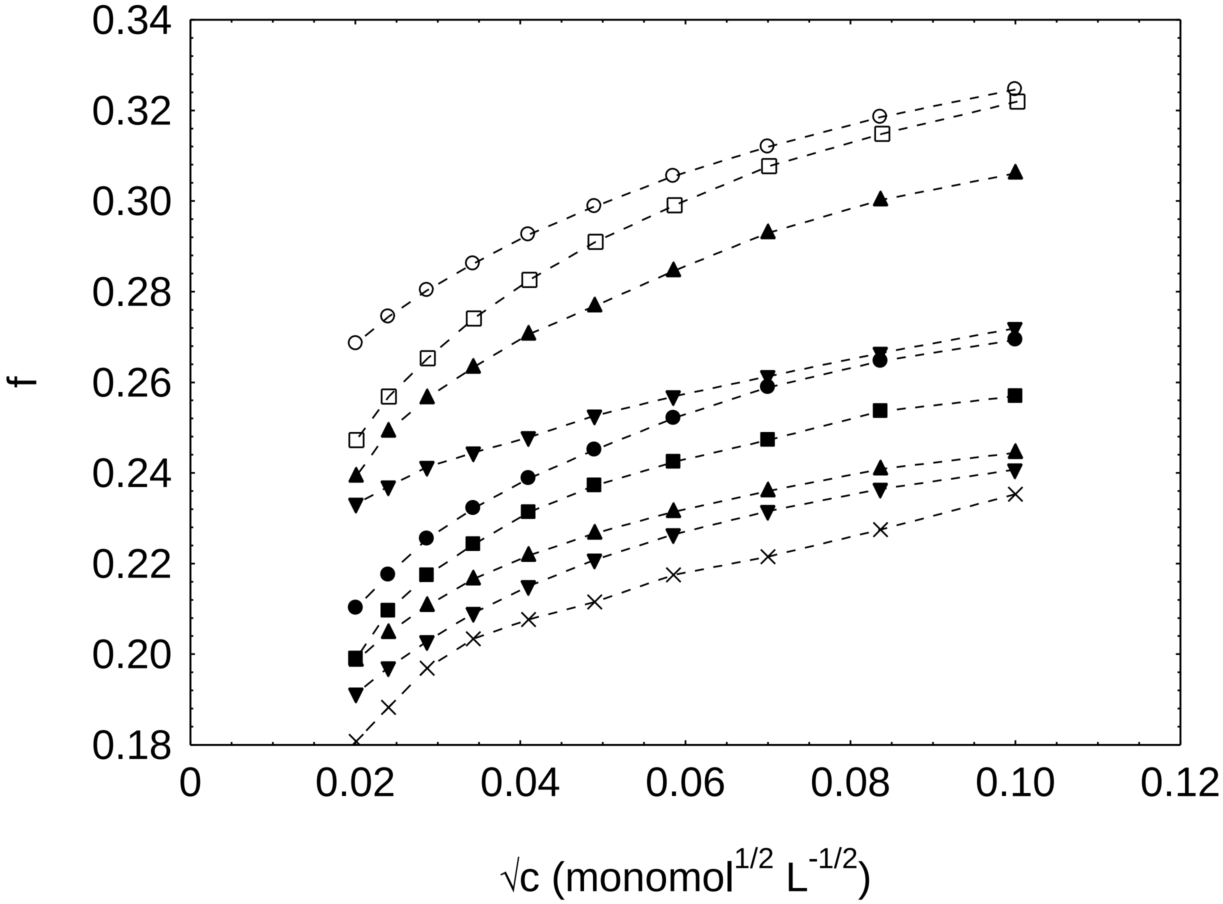


Fig. 3(b) Fraction of free counterions in aqueous solution of NaPSS (molecular weight = 1000000) in presence of NaCl at different temperatures. For the significance of symbols, please refer to Fig. 3(a).

particular reference to the effect of polyelectrolyte molecular weight which has not been investigated earlier.

The fractions of free counterions are found to increase as the polyelectrolyte concentration is increased for all the NaPSS-NaCl systems under investigation (Figs. 3 and 4). Higher degree of dissociation of counterions with increasing polyelectrolyte concentration might be attributed to a variation of the dielectric constant with polyelectrolyte concentration. Owing to the polarizability of the polyelectrolyte, the dielectric constant of the medium is known to increase as the

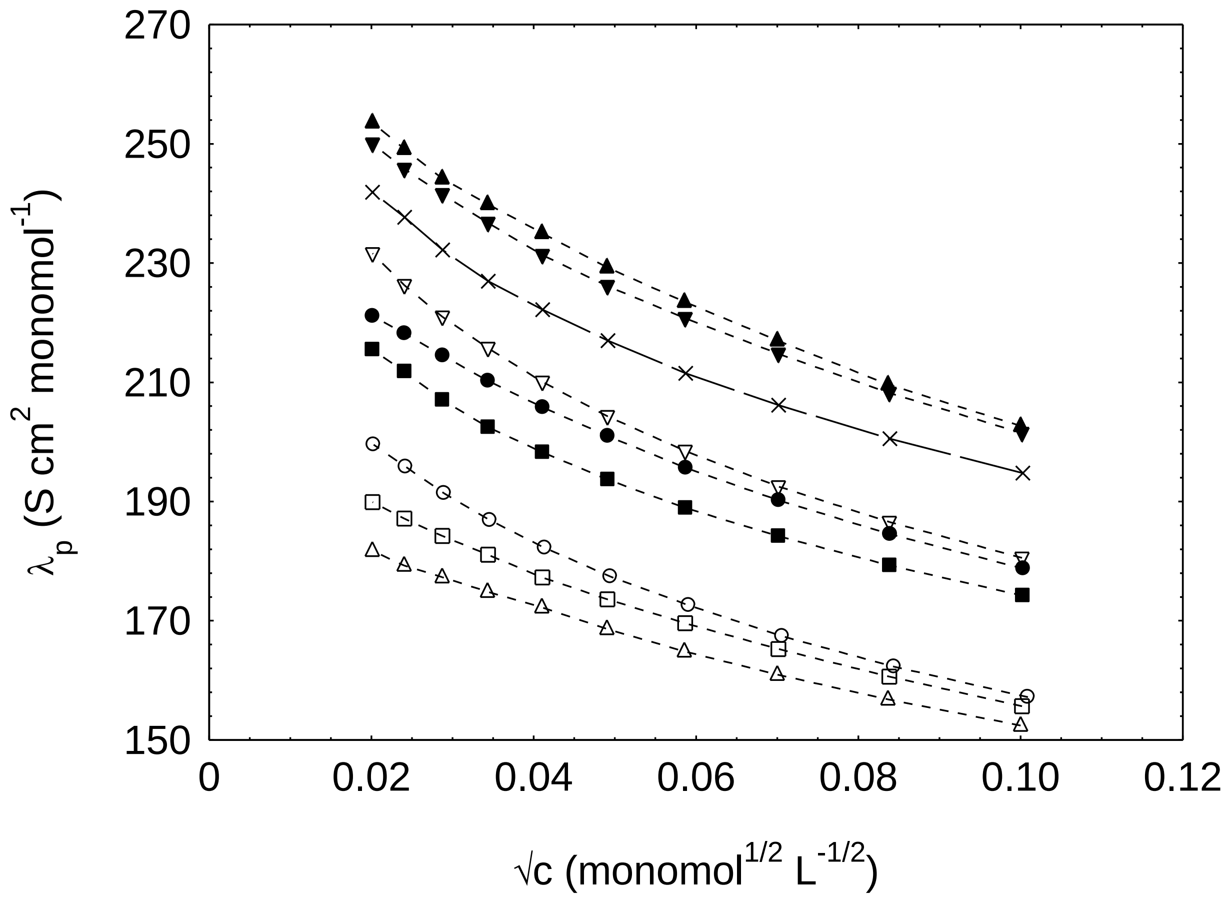


Fig. 4(a) Polyion equivalent conductivity in aqueous solution of NaPSS (molecular weight = 70000) in presence of NaCl at different temperatures. For the significance of symbols, please refer to Fig. 3(a).

polyelectrolyte concentration is increased.[44] Although the polyelectrolyte concentration-dependent increase in the effective dielectric constant of the medium has not yet been completely understood,[45] the experimental evidence is now well established.[44,46] For NaPSS in particular, the frequency-dependent dielectric constant of the medium has been shown to increase with NaPSS concentration.[47] The increase in dielectric constant value will cause a reduction in the Bjerrum length. Now, since the Bjerrum length sets the length scale for the separation between the dissociated sites on the polyion chain,[18,44,48] there will be lower level of counterion condensation with the increase in the dielectric constant of the medium. Obviously, this effect becomes more

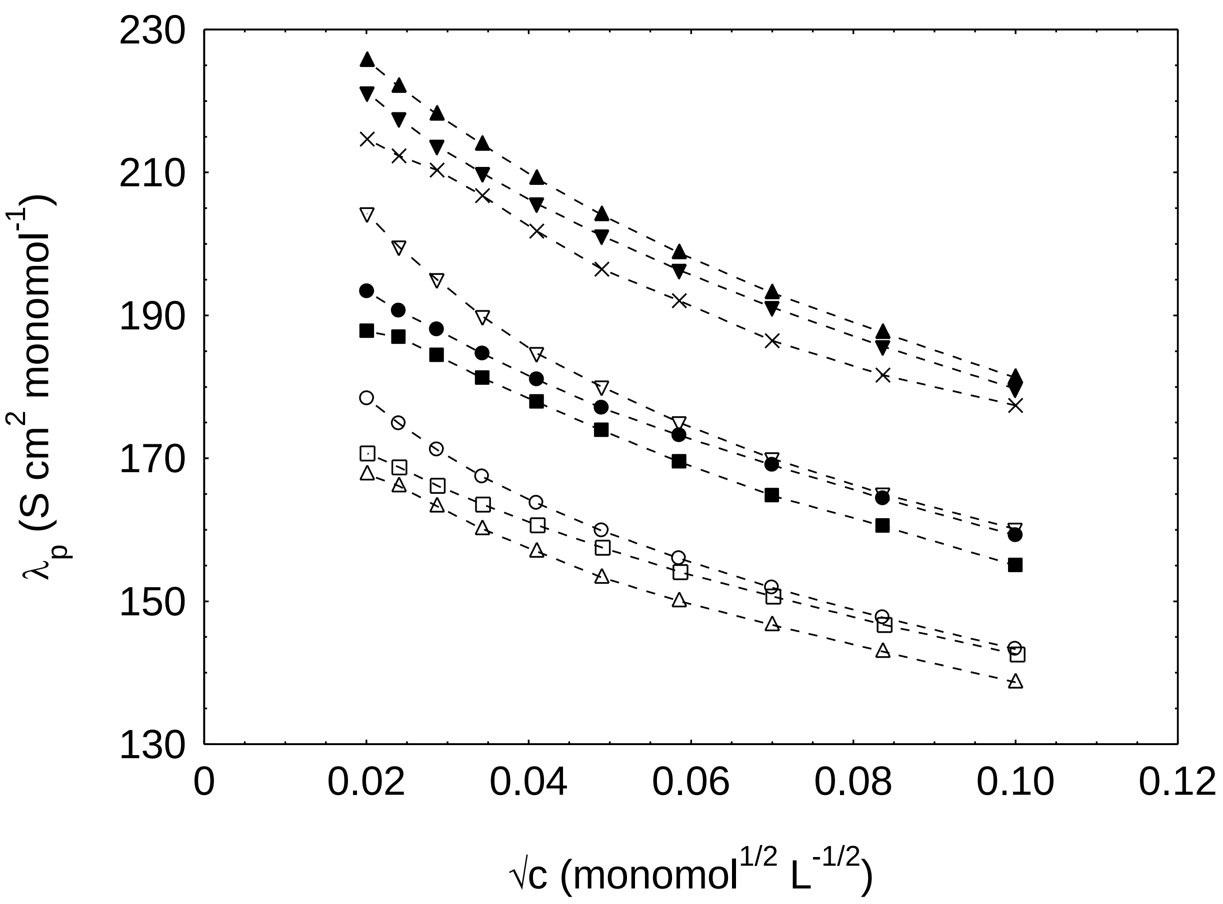


Fig. 4(b) Polyion equivalent conductivity in aqueous solution of NaPSS (molecular weight = 1000000) in presence of NaCl at different temperatures. For the significance of symbols, please refer to Fig. 3(a).

important at higher polyelectrolyte concentrations. Further theoretical work on the polarizability of polyelectrolytes is, however, still awaited for a detailed quantitative description of the conductivity of polyelectrolyte solutions at high concentration.

Figs. 3(a) and (b) reveal a decrease in the fraction of free counterions as the temperature is increased over the entire polyelectrolyte concentration region for any given NaPSS-NaCl system. This observation may be ascribed to a variation in hydration and, hence, a concomitant alteration in the condensation behavior of the counterions as the temperature changes. Elevation of temperature causes a gradual dehydration of the counterions as well as of the dissociated sites on the polyion chain; this would result in more condensation of counterions on the polyion as there will be greater electrostatic attraction between the dehydrated ionic species with higher surface charge densities as the temperature is raised. This is amply demonstrated by the lower degree of counterion condensation at higher temperatures. Dehydration of the sodium ions at higher temperatures has already been inferred in an earlier investigation where the mobility of sodium ions was found to increase appreciably with temperature.[49] Similar behavior was also observed with sodium polystyrenesulfonate[29] and sodium carboxymethylcellulose[30] in mixed-solvent media earlier.

The higher molecular weight NaPSS sample manifests a higher degree of counterion condensation than its lower molecular weight counterpart over the investigated polyelectrolyte concentration range at any given temperature and in presence of a given amount of the added salt (*cf*. Figs. 3(a) and (b)). The charge density parameter has nothing to do with the observed difference since it is the same for both the polymer samples. This may, however, be interpreted in terms of the confinement of more counterions in the more coiled structure of the higher molecular weight polymer sample in comparison with its lower molecular weight fraction. There has, so far, been only one report on the polyelectrolyte molecular weight dependence of the fraction of free counterions in salt-free polyelectrolyte solutions.[15] Influence of polyelectrolyte molecular weight on the counterion condensation behavior in salt-containing polyelectrolyte solutions, however, has not been yet investigated. The present study, therefore, reports for the first time the polyelectrolyte molecular weight dependence of the counterion condensation phenomena in polyelectrolyte-salt solutions.

Polyion equivalent conductivity. An inspection of the effects of polyelectrolyte concentration, added salt concentration, the experimental temperature and the polyelectrolyte molecular weight on the equivalent conductivity (λ_p) of the polyion (*cf*. Figs. 4(a) and 4(b)) helped provide an important insight as to the relative role played by the effective charge and size of the monomer units in determining the polyion equivalent conductivities.

The polyion equivalent conductivity is found to decrease as the concentration of the added salt increases and also as the molecular weight of the polyelectrolyte increases. As discussed earlier, there would be more counterion condensation and hence less effective charge on the monomer units either with the increase in the concentration of the added salt or with the increase in the molecular weight of the polymer sample. It, thus, appears that a decrease in the charge of the monomer units alone might have caused the reduction of the polyion equivalent conductivity. On this basis, the dependence of the polyion equivalent conductivity on the polyelectrolyte concentration or on the experimental temperature seems to be anomalous, where with the increase in the polyelectrolyte concentration, although the effective monomer charge increases (please see above), there is a reduction in polyion equivalent conductivity, and with the increase in the experimental temperature, although the monomer charge decreases (please see above), there is an increase in polyion equivalent conductivity. These observations can be interpreted if both the effective monomer size and effective monomer charge are simultaneously taken into consideration. It may be noted that while increasing effective monomer size should cause an increase in the polyion equivalent conductivity, an increase in the monomer size should result in a reduction in it, and it is the subtle balance between these opposing effects which would decide the observed mobility in the present NaPSS-NaCl aqueous solutions. The results obtained thus indicated clearly that the charge effect predominates over the size effect when either the added salt concentration or the polyelectrolyte molecular weight is varied, whereas the size effect overrides the charge effect when either polyelectrolyte concentration or temperature is varied.

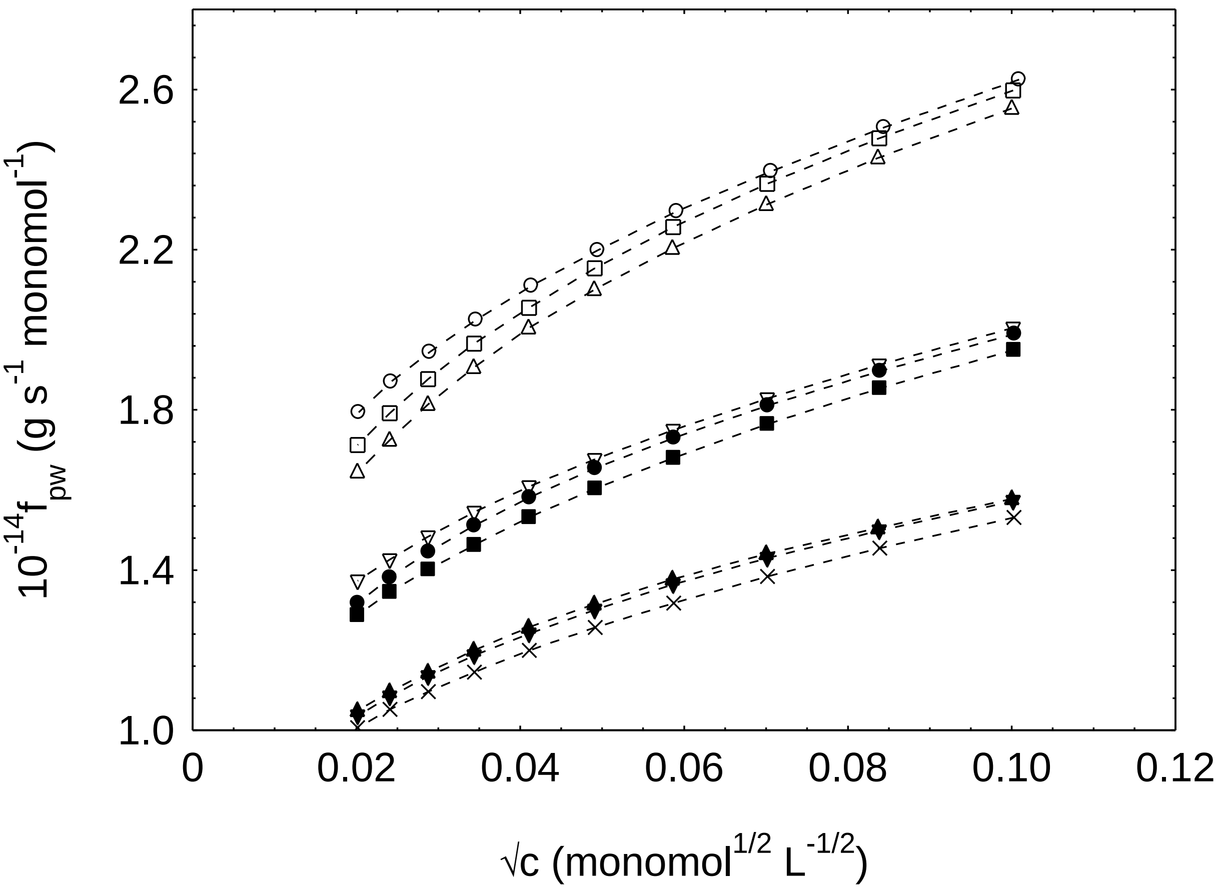


Fig. 5 (a) Coefficient of friction between polystyrenesulfonate ion and the solvent in aqueous solution of NaPSS (molecular weight = 70000) in presence of NaCl at different temperatures. For the significance of symbols, please refer to Fig. 3 (a).

Coefficient of friction between the polyion and the solvent (f_{pw}). Considering that the charge of the polyion is partly screened by the atmospherically bound counterions, the force of the external electric field per monomer unit is supposed to be reduced to the fraction f of its value in absence of counterions.[50] According to this assumption, the hydrodynamic friction coefficient per mole of monomer units, f_{pw}, can be obtained from the relation[51]

$$f_{pw} = \frac{|z_p| f F^2}{\lambda_p} \tag{18}$$

where z_p is the number of elementary charges on each monomer unit of the fully dissociated polyion chain, while the significance of other symbols has been mentioned earlier.

Figs. 5(a) and (b) show the effects of the molecular weight of the polyelectrolyte, added salt concentration and temperature on the f_{pw} *vs.* $\sqrt{c}$ profiles.

A delicate balance of three important factors, namely the effective monomer size, the effective monomer charge, and the presence of other species if any, in the aqueous environment governs the value of the coefficient of friction between the polyion and the solvent molecules. These factors will be taken into account in order to interpret the present observations.

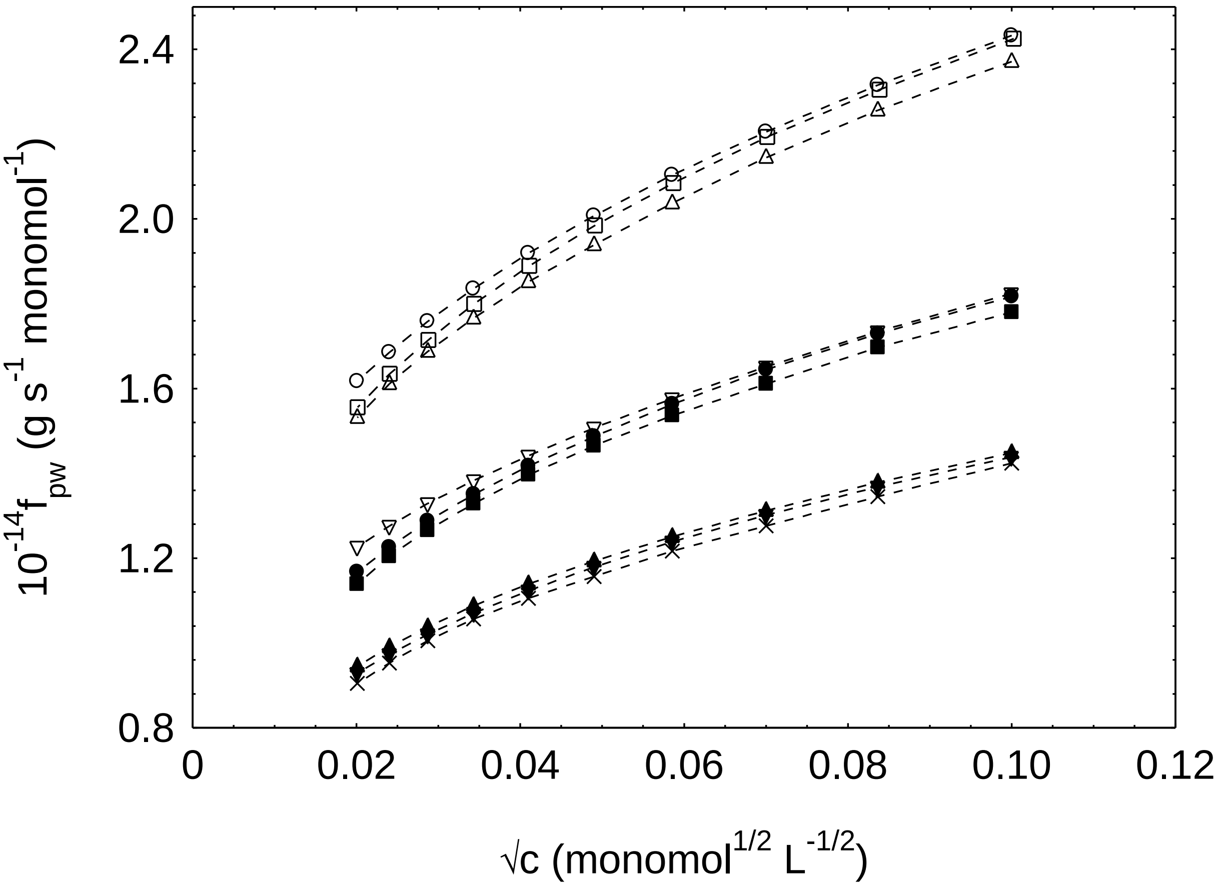


Fig. 5 (b) Coefficient of friction between polystyrenesulfonate ion and the solvent in aqueous solution of NaPSS (molecular weight = 1000000) in presence of NaCl at different temperatures. For the significance of symbols, please refer to Fig. 3 (a).

A significant increase in the coefficient of friction value of the polystyrenesulfonate ion as a function of the polyelectrolyte concentration was observed in presence of a given amount of the added salt in a solution of a polyelectrolyte with a particular molecular weight and at a particular temperature. Both the monomer charge and the monomer size have been shown to increase as the concentration of polyelectrolyte increases. Both these factors would, of course, cause a greater frictional resistance between the monomers and the solvent molecules in their vicinity at higher polyelectrolyte concentrations.

The monomer units are found to experience lower friction the higher the concentration of the added salt (NaCl) over the entire polyelectrolyte concentration range. Addition of NaCl to a polyelectrolyte solution of a particular concentration leads to a reduction both in charge and the size of the monomer units, and this would result in a consequent decrease in the friction of the monomer units with the solvent molecules.

An elevation of temperature is found to reduce the frictional resistance of the monomers with the solvent molecules in a specified polyelectrolyte solution provided the polymer molecular weight remains the same. Increasing temperature induces more counterion condensation thus causing polyion chain contraction, *i.e.*, there is a reduction both in monomer charge and monomer size upon temperature elevation and hence gives rise to weaker frictional resistance. This supports the phenomenon of gradual dehydration of the monomer units as inferred earlier.

A significant decrease in the friction coefficient with increasing molecular weight of the polymer over the entire polyelectrolyte concentration range in presence of a given amount of the added salt at a given temperature was also observed. Here, the fraction of free counterions and hence the charge on the monomer units decrease with increasing molecular weight. This would result in a reduction in the effective monomer size. Hence the coefficient of friction would also decrease with increasing polyelectrolyte molecular weight.

Conclusions

The interaction between a polyelectrolyte sodium polystyrenesulfonate and sodium chloride in aqueous milieu has been investigated using electrical conductivity data coupled with a recently developed model using the scaling description for the conformation of a polyion chain. Higher level of counterion condensation takes place with decreasing polyelectrolyte concentration, increasing temperature, increasing polyelectrolyte molecular weight and increasing added salt concentration. Increasing polyelectrolyte concentration caused an increase in the dielectric constant of the medium with a concomitant reduction in counterion condensation. Higher temperatures led to a dehydration of counterions and hence to a higher level of counterion condensation. The variations of polyion equivalent conductivity with polyelectrolyte concentration, concentration of the added salt, experimental temperature, and the polyelectrolyte molecular weight have been interpreted considering simultaneously the roles of the effective monomer size and effective monomer charge. In the present system, the variation of polyion equivalent conductivity with the added salt concentration or with the polyelectrolyte molecular weight is governed by the charge effect, while that with the polyelectrolyte concentration or with the temperature is governed by the size effect. The values of the coefficient of friction of the monomer with the solvent molecules are governed both by the monomer charge and the monomer size. It has been demonstrated that the coefficients of friction increase with increasing polyelectrolyte concentration, whereas these decrease either with an increase in the temperature, or an increase in the concentration of the added salt, or with the increase in the polyelectrolyte molecular weight. The present study provided new insight into the effects of polyelectrolyte molecular weight on the fractions of free counterions, the polyion mobility and the monomer-solvent friction coefficients in polyelectrolyte-salt solutions, which was not investigated earlier.

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