Communications to the Editor

Temperature Dependence of the Electrolytic Conductivity of Poly(styrenesulfonate) Solutions

Useful insights into the complex physicochemical behavior of polyelectrolyte solutions have been provided by systematic studies of the influence of a variety of characteristic properties in a few selected polyelectrolyte systems.[1,2] Extensive studies of poly(styrenesulfonate) solutions carried out in this laboratory have been reviewed some time ago.[3] Considering the relatively weak temperature dependence of the predominant electrostatic interactions, the temperature effects on the thermodynamic properties were usually supposed to be of minor importance and have, so far, been paid less attention. Osmotic pressures of poly(styrenesulfonate) solutions measured at room temperatures by vapor pressure or membrane osmometry have indeed been found to compare favorably with the cryoscopic results. More interesting temperature effects eventually revealing the non-Coulombic contributions to the excess thermodynamic quantities have been observed in recent calorimetric studies of the same system.[4] Significant influence of the temperature is, however, expected to be found in the case of the transport properties due to the pronounced temperature dependence of the viscosity of water, which mainly determines individual ionic mobilities as well as the hydrodynamic interactions among ions. In the present work a preliminary examination of the effect of the temperature on the electrolytic conductivity of aqueous poly(styrenesulfonate) solutions is reported. The molar conductivities of the poly(styrenesulfonic acid) (poly[1-(4-sulfophenylethylene)]) (HPSS) and its sodium (NaPSS) and magnesium salts (MgPSS) are determined as functions of the concentration at different temperatures ranging from 0 to 40 °C. The Walden rule is shown to apply approximately to the overall conductivity of the two polysalts as well as to the molar conductivity of the polyion. The estimated relaxation effect on the conductivity, presumably mainly determined by the equilibrium structure of the polyelectrolyte solution,[2,5] is found not to depend on the temperature within the accuracy attained.

A ca. 0.02 monomolal solution of sodium poly(styrenesulfonate) (NaPSS) with a nominal molecular weight of $\sim 7 \times 10^4$ and the degree of sulfonation 1.00, supplied by Polyscience, Inc., was first purified by filtration through the membrane filter and then by dialysis.[6] The acid and its magnesium salt were then obtained from NaPSS by ion exchange. Distilled water of specific conductivity below 1.2×10^{-6} Ω^{-1} cm^{-1} at 25 °C was used to prepare the solutions. The conductivity was measured by the Jones conductance bridge (Leeds & Northrup Co.) at temperatures of 0 ± 0.02, 15 ± 0.02, and 40 ± 0.02 °C within the concentration interval from 10^{-4} to about 0.14 monomol dm^{-3}. The measurements were performed at four different frequencies ν, and the conductivities extrapolated to $\nu = \infty$ were used as final results, although the frequency dependence was generally of minor importance. The average accuracy in the molar conductivity was estimated to be about ±0.5% at concentrations above 5×10^{-3} monomol dm^{-3}, eventual errors being mainly due to the uncertainties in the polyelectrolyte concentrations.

The concentration dependence of the molar conductivity λ of NaPSS, MgPSS, and HPSS at different temperatures is shown in Figures 1–3. The data for 0, 15, and 40 °C are from this work, whereas the curves for 25 °C are taken from earlier studies.[7–9] A few additional measurements at 25 °C have also been made to verify that the literature data can be reproduced with the samples used in this study. Obviously, the concentration dependence of the molar conductivity follows one and the same pattern at all the temperatures considered. The differences found seem to result mainly from the viscosity variation. At the four temperatures chosen, the viscosity of water has the following values: η = 1.792 cP at 0 °C, 1.14 cP at 15 °C, 0.8937 cP at 25 °C, and 0.656 cP at 40 °C.[10] The products $\lambda\eta$ of the three poly(styrenesulfonates), determined as functions of the concentration at different temperatures, are shown in Figure 4. The Walden rule $\lambda\eta$ = const is found to hold approximately for the polysalts, NaPSS and MgPSS, while it could not be expected with the polyacid because of the peculiar mechanism of the hydrogen ion migration. If the individual mobilities of the polyion and of the counterions followed the Stokes' law $u_i \propto \eta^{-1}$ and the electrophoretic retardation was supposedly inversely proportional to η, the observed behavior would indicate that the relaxation effect on the conductivity does not essentially depend on the temperature. In a number of preceding works[7–9,11–13] the relaxation effect has been estimated from the conductivity and transport numbers or, alternatively, from the comparison of the molar conductivities of polyelectrolytes sharing the common polyion.[2,11,14–16] In the latter approach, the approximate relation

$$\gamma = 1 + \frac{\Delta E}{E} \cong \frac{\lambda_1 - \lambda_2}{\lambda_1^\circ - \lambda_2^\circ} \qquad (1)$$

is obtained by assuming that both the relaxation ratio γ and the electrophoretic effect depend only on the valency but not on the other properties of the counterions. Above, λ_i is the molar conductivity of the polyelectrolyte with the counterions having the limiting ionic conductivity λ_i° and γ is the ratio of the mean field strength experienced by an individual ion and the external field E. The nonideal behavior of polyelectrolyte solutions is sometimes interpreted in terms of the so-called two-state model considering that the counterions can occupy two discrete states, free or bound to the polyion. In this approximation γ can be related to the fraction of the unbound counterions.[2] Despite the inherent approximations, discussed in some more detail in ref 2, eq 1 was applied to provide the first estimate of the relaxation factor γ in the present work. In Table I, the values of γ obtained from the molar conductivities of HPSS and NaPSS measured at 0 and 25 °C are listed. A comparison between the values of γ determined separately for NaPSS[8,9,17] and for HPSS[7,12] from the conductivity and transport numbers measured at 25 °C, reported previously, reveals that γ depends on the choice

Table I
Concentration Dependence of the Relaxation Factor γ and the Polyion Conductivity λ_- at T = 0 and 25 °C

c, monomol dm^{-3}	γ(25 °C)	γ(0 °C)	λ_-(25 °C)	λ_-(0 °C)	W^a
0.01	0.415	0.406	40.7	18.8	1.08
0.02	0.444	0.440	35.4	15.9	1.11
0.04	0.479	0.482	30.2	13.7	1.10
0.06	0.505	0.518	28.2	12.5	1.12
0.08	0.524	0.529	26.0	13.2	0.98
0.10	0.540	0.537	25.1	13.4	0.94
0.12	0.546	0.545	25.6	13.5	0.95

[a] Defined in eq 2.

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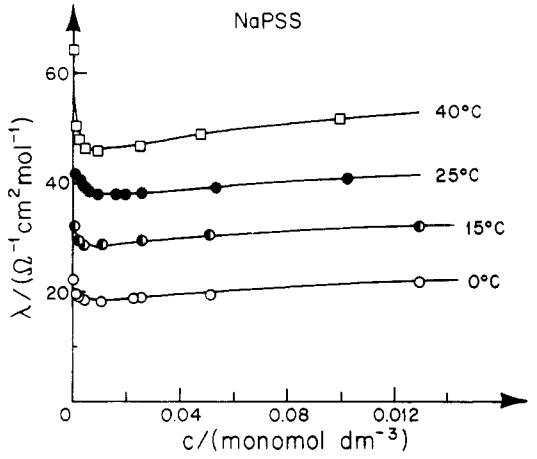

Figure 1. Concentration dependence of the molar conductivity of sodium poly(styrenesulfonate) at different temperatures.

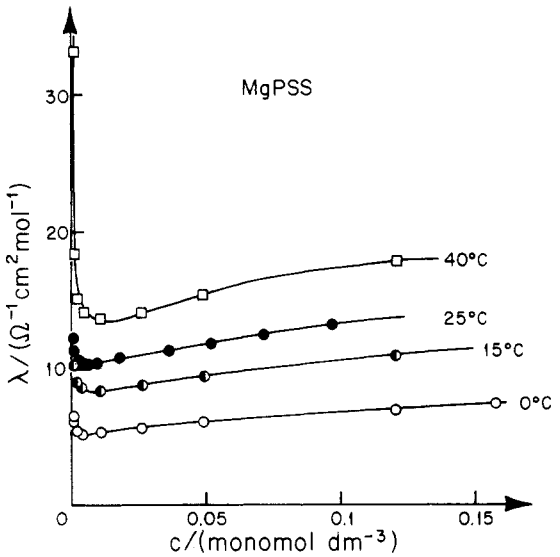

Figure 2. Concentration dependence of the molar conductivity of magnesium poly(styrenesulfonate) at different temperatures.

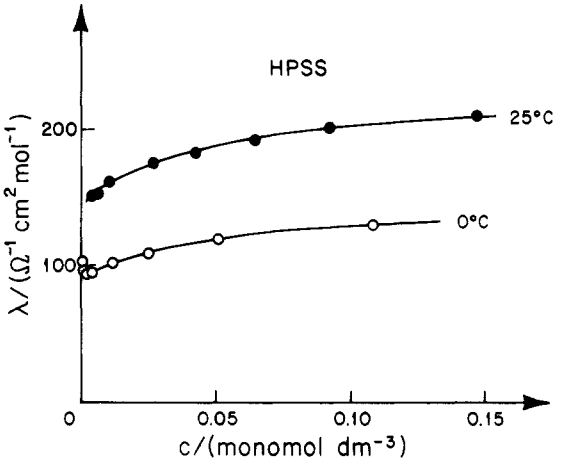

Figure 3. Concentration dependence of the molar conductivity of poly(styrenesulfonic acid) at 0 and at 25 °C.

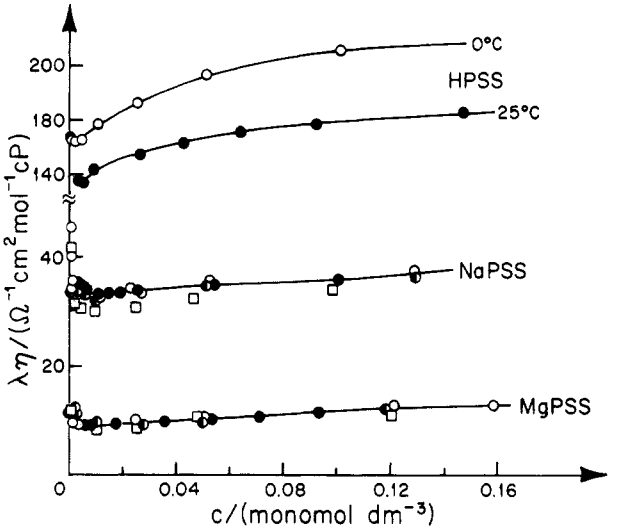

Figure 4. Concentraction dependence of the product $\lambda\eta$ in NaPSS, MgPSS, and HPSS solutions at 0 °C (○), 15 °C (◐), 25 °C (●), and 40 °C (□).

of the counterion to a certain extent and is 5–10% higher in HPSS than in NaPSS solutions. It is therefore not surprising that eq 1 based on the assumption $\gamma_{NaPSS} \sim \gamma_{HPSS}$ predicts values of γ which are up to 10% too high if compared to those determined at 25 °C earlier.[12,17] The comparison with the coefficients of self-diffusion of the counterions as determined by the Fourier transform NMR spectrometry[18] is somewhat more favorable. In conformity with former studies of the system[17,19,20] λ and γ exhibit positive deviations from the limiting laws of the line charge model[21,22] for the polyion charge density characteristic of PSS solutions, the experimental values of γ being closer to the results of the cylindrical cell model[23] given in the preceding work.[18] It is interesting to observe the apparent independence of the relaxation factor γ on the temperature.

The electrostatic contribution is mainly determined by the value of the product ϵT which varies less than 3% within the interval 0–25 °C, and the resulting temperature effect is probably smaller than the accuracy of the method. The presence of eventual significant non-Coulombic interactions would, however, most likely lead to a measurable temperature dependence of γ.

Knowing the molar conductivity λ and the relaxation factor γ, it is also possible to estimate the polyion conductivity λ_-. In accordance with eq 1 the molar conductivity of a polyelectrolyte can be related to λ_- by the expression $\lambda = \gamma(\lambda_- + \lambda_+^\circ)$. As with eq 1 the ionic conductivities of the counterions were approximated by the corresponding values at infinite dilution.[10,24] The polyion conductivity obtained in this way still contains the electrophoretic contribution which, as can be seen from the results obtained from NaPSS and HPSS conductivities and listed in Table I, increases with the concentration. The uncertainties due to the inaccuracy in the values of γ could not be avoided in this approach. Considering that both the isolated polyion mobility[25] and the leading contribution to the electrophoretic retardation[26] are, to a good approximation, inversely proportional to the viscosity of the solvent, η, the product $\lambda_-\eta$ should not depend on the temperature T. In the last column of Table I the products

$$W(T_1,T_2,c) = \lambda_-(T_1,c)\eta(T_1)\lambda_-(T_2,c)^{-1}\eta(T_2)^{-1} \quad (2)$$

at different concentrations are given. Small deviations of the above product from unity indicate the approximate validity of Walden rule for polyion conductivity. A more general statement would, however, be possible on the basis of additional experimental data, including reliable ionic conductivities obtained by transport-number measurements at different temperatures. More remains to be done in the theory before interpretations of polyelectrolyte conductivity comparable to those of simple electrolytes will become possible. The Smoluchowski level of description

of transport phenomena developed for the treatment of ordinary electrolytes[26] seems to possess sufficient generality[27] with some underlying simplifications to be reexamined. Still, the pecularities related to the lower symmetry of ionic distributions and to the effect of at certain conditions rather rapid reorientation of the polyions or of the segments of them[28] should be properly incorporated. A more detailed picture of the structure of the solution and in particular of the mutual distribution of the polyions or their segments in equilibrium has also to be known before the fluctuations around it can be studied.

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Electron Spin Resonance Evidence for Specific Solvation Effects in Ionomer Solutions

The solution properties of ionomers are complex and depend on the polymer concentration, the nature of the anion and the cation, the temperature, and the solvent. Relatively few studies have considered how the polarity of the solvent affects the behavior of an ionomer in solution.

Schade and Gartner[1] compared the solution behavior of ionomers derived from copolymers of styrene with acrylic acid, methacrylic acid, and half-esters of maleic acid in tetrahydrofuran (THF), a relatively nonpolar solvent, and dimethylformamide (DMF), a polar solvent.[2] In DMF, they observed a polyelectrolyte effect at low polymer concentrations for Na salts, which they attributed to ionization of the carboxyl group. The increase in the reduced viscosity at very low polymer concentrations is a result of chain expansion due to electrostatic repulsive forces between unshielded anions. With a solvent of lower dielectric constant, such as THF, no dissociation of the ion pair occurs and no polyelectrolyte effect was observed.

Recently several other studies[3-6] have been reported concerning the effect of solvent polarity on the dilute solution viscosity of ionomers. Most of these studies used THF as the nonpolar solvent and DMF as the polar solvent. Lundberg and Phillips[4] studied the solution properties of sulfonated polystyrene (SPS) ionomers in solvents with dielectric constants ranging from 2.2 (dioxane) to 46.7 (Me_2SO). These authors concluded that polar solvents tend to solvate the ions, whereas nonpolar solvents promote ion pairs and interactions between the ionic dipoles.

All the previous studies of ionomer solutions have relied strictly on rheological measurements. Spectroscopic measurements that directly probe the local interactions have not been reported, and such experiments are clearly warranted in view of the complicated solution behavior of these materials. In this communication, we report some electron spin resonance (ESR) results for Mn(II) salts of SPS. Other ESR and infrared spectroscopy studies of these ionomers are reported elsewhere.[7,8]

The SPS ionomers used in this study were prepared from a commercial polystyrene that had a number-average molecular weight of 101 000 and a weight-average molecular weight of 206 000. The procedure of Makowski et al.[9] was used to prepare sulfonated polystyrene containing 2.25 mol % sulfonic acid groups that were converted to the Mn(II) salt by neutralization with manganese acetate. Electron spin resonance (ESR) measurements were made with a Varian E-102E spectrometer at X-band frequency with 100-kHz field modulation. The frequency (ν) was measured with a Varian wavemeter with a crystal detector.

The ESR spectra for 0.5 wt % solutions of MnSPS in THF and DMR are shown in Figure 1. The sharp six-line spectrum for DMF is typical of isolated Mn(II) ions in solution.[10] This result indicates that DMF is able to solvate the dipole interaction to the extent of isolating the Mn(II) ions. Previous infrared spectroscopy (IR) studies[7] also showed that DMF solvates the ion pair, removing the cation from the anion environment. These results are consistent with the observation of a polyelectrolyte effect for SPS in DMF.[4,6] For the THF solution, only a single broad line ESR spectrum is observed. The disappearance of the structure in the spectrum is due to magnetic interactions that occur only in concentrated systems, such as in the case of cation association. This result for SPS in THF is consistent with the absence of a polyelectrolyte effect for this system.[4,6]

Lundberg and Phillips[4] reported that the addition of

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