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Determination of Polyelectrolyte Charge and Interaction with Water Using Dielectric Spectroscopy

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ABSTRACT: Using the dielectric strength and relaxation time of a high-frequency (1 MHz−1 GHz) dielectric relaxation, we estimate the effective charge on polyelectrolytes and their net thermodynamic repulsive interaction with solvent. The utility of this method is demonstrated for semidilute aqueous solutions of the sodium salt of several sulfonated polyelectrolytes of varying charge and strength of repulsive interaction with water, with no added salt. At high concentrations, as the concentration is increased, the effective charge of strongly charged polyelectrolytes always *increases*, as previously observed in conductivity and osmotic pressure measurements. Interestingly, we find that the effective polymer−solvent repulsion increases in direct proportion to the effective charge on the polyelectrolyte chains. This proportionality means that, although the additional charge would increase the contour length of the chain of electrostatic blobs, the increase in repulsion between solvent and polymer offsets this effect, making the contour length of the chain essentially independent of polyelectrolyte concentration. This then explains why the correlation length of semidilute polyelectrolyte solutions fortuitously agrees with simple scaling predictions.

I. Introduction

Polyelectrolyte solutions are not as well understood as solutions of polymers that do not bear charges, despite considerable research on polyelectrolytes over the past 50 years. We propose that a large part of the reason for slow progress in this field is that experimentalists often do not measure either the effective charge on the chain or the thermodynamic interaction of the chain with the solvent. The standard assumption is that both of these are independent of polyelectrolyte concentration. In this paper we present evidence that this assumption is wrong and suggest an interpretation of a simple dielectric experiment to directly measure both of these crucial parameters. In water, these two parameters are found to be proportional to each other. This proportionality creates a mutually offsetting net effect on the scattering function, which is known to be insensitive to charge density.[1] Our results imply that dielectric spectroscopy is a powerful way to estimate both the effective charge density and the thermodynamic interaction parameter, which are every bit as important for polyelectrolyte solutions as measuring chain length. Hopefully, an improved understanding of polyelectrolyte solutions will result.

For several years, a paradox has been recognized for the static properties of polyelectrolyte solutions with no added salt.[3,4] While small-angle neutron scattering measures a correlation length that agrees reasonably with scaling predictions, osmotic pressure and conductivity measurements *in the same range of concentration* clearly show that the effective charge on the chain is increasing as concentration increases. Figure 1 shows the published SANS (small-angle neutron scattering) data for the correlation length of NaPSS[2] (the sodium salt of sulfonated polystyrene) and NaPAMS[3] (the sodium salt of poly(2-acrylamido-2-methylpropanesulfonate)), determined as $\xi = 2\pi/q^*$, with q^* the wavevector at which the scattering function has a local maximum. The subtle differences in correlation length are beyond experimental error and reflect the slight differences between these two polymers. However, both polymers demonstrate the simple scaling for the correlation length ξ expected by de Gennes et al.,[5] namely, a reciprocal-square-root dependence on concentration.

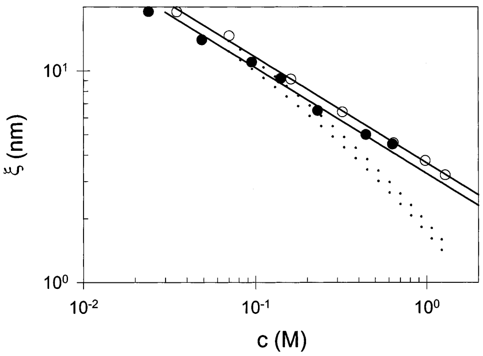

Figure 1. Concentration dependence of the correlation length determined by SANS ($\xi = 2\pi/q^*$, where q^* is the wavevector of a local maximum in the scattered intensity) for NaPAMS[1] (open circles) and NaPSS[2] (filled circles). The dashed lines are fits to eq 1 (with slope required to be $-1/2$). The dotted curves are predictions of eq 1 with the empirical concentration dependence of f from the data in Figure 2 and assuming τ is independent of concentration.

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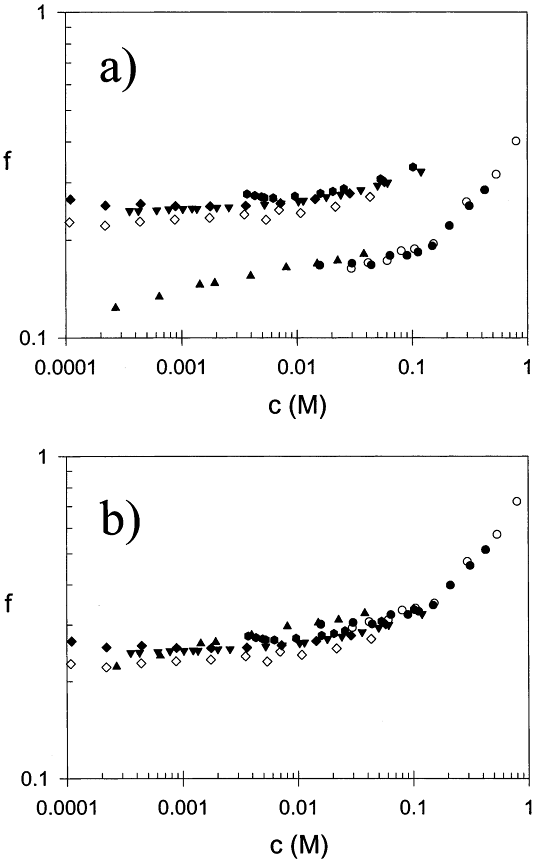

Figure 2. (a) Concentration dependence of the fraction of charged monomers determined by osmotic pressure Π (eq 2) and specific conductance Λ (eqs 3 and 4) for NaPSS (filled circles from Π,[3] filled triangles from Π,[8] filled upside-down triangles from Λ,[9] filled hexagons from Λ,[10] and filled diamonds from Λ[7]) and NaPAMS (open circles from Π,[3] open diamonds from Λ[7]). (b) Same as (a) but with the osmotic pressure determinations of *f* multiplied by a factor of 1.8.

$$\xi = \frac{\tau^{1/2}}{f^{2/3} l_B^{\ 1/3} b^{1/6} c^{1/2}} \tag{1}$$

The above equation is specifically for a polyelectrolyte in a poor solvent for the uncharged polymer;[6] $\tau \equiv (\theta - T)/\theta$ is the solvent quality parameter (a reduced temperature), θ is the temperature at which the net excluded volume for the monomer is zero, f is the fraction of monomers bearing an effective charge that is not neutralized by a condensed counterion, $l_B \equiv e^2/\epsilon_w kT$ is the Bjerrum length (e is the elementary charge, ϵ_w is the dielectric constant of water, k is Boltzmann's constant, T is absolute temperature), b is the monomer size, and c is the polymer concentration (number density of monomers). The fits of eq 1 to the SANS data in Figure 1 are shown as the solid lines. While the departures are slightly beyond experimental error, they are very small, leading to the preliminary conclusion that the scaling theory is reasonable. However, the prediction of eq 1 is based on the assumption of an effective charge that is independent of concentration. Figure 2 shows the apparent fraction of charged monomers f determined from osmotic pressure[6] Π using eq 2 and from specific conductance[7] Λ using eqs 3 and 4 (which also relies on the measured correlation length).

$$f = \frac{\Pi}{ckT} \tag{2}$$

$$f = \frac{\sqrt{\lambda_c^{\ 2} + 4\lambda_p\Lambda} - \lambda_c}{2\lambda_p} \tag{3}$$

$$\lambda_p = \frac{c\xi^2 e^2 \ln(\sqrt{\tau/(cb^3)})}{3\pi\eta_s} \tag{4}$$

The counterion specific conductance is λ_c (sodium has $\lambda_c = 50$ S cm^2/mol), e is the elementary charge, and η_s is the solvent viscosity. The counterion contribution to specific conductance is $f\lambda_c$, and the polyion contribution to specific conductance is $f^2\lambda_p$. Both conductivity and osmotic pressure suggest an increase in f as polyelectrolyte concentration becomes large, and the increase starts at the same concentration (roughly 0.1 M) for f evaluated from both properties.

An increase in osmotic pressure is expected at sufficiently high polyelectrolyte concentration that could account for the increase in f due to the polymer effect. Polymers contribute kT per correlation blob to osmotic pressure. At low polyelectrolyte concentrations, the polymer contribution is negligible compared with the contribution from free counterions (eq 2 is based on kT per free counterion) because there are many more free counterions than correlation blobs. At very high polyelectrolyte concentration, there will be more blobs than free counterions, and the polymer effect will dominate osmotic pressure. The crossover concentration separating these two regimes corresponds to one free counterion per blob, which would not occur until much larger concentrations than the data range of Figure 2. At the estimated concentration of 0.1 M where f starts to increase, the correlation length is roughly 10 nm, and there should be of order 20 free counterions per correlation blob. Hence, the increase in f *cannot* be attributed to a polymer effect and instead suggests an actual increase in the fraction of free counterions in solution. The origin of the discrepancy in estimations from conductivity and osmotic pressure (Figure 2a) is elucidated in the Discussion section. For comparison, we simply shift the osmotic pressure estimates of f upward by a factor of 1.8, resulting in Figure 2b. This shift is not entirely unexpected, as the Katchalsky cell model[11] predicts $f = 2\Pi/(ckT)$.

If f were the only parameter changing, the correlation length should not obey eq 1. Using the apparent $f(c)$ in Figure 2b to describe the fraction of monomers bearing an effective charge, we would expect the correlation length to obey the dotted curves in Figure 1. Clearly, this is *not* observed, and at first glance Figures 1 and 2 appear inconsistent with one another. The principal purpose of the work reported here is to resolve this apparent inconsistency. In so doing, we will also expand upon Ito's interpretation of a megahertz dielectric relaxation of polyelectrolyte solutions with no added salt[12] to allow estimation of both the fraction of charged monomers f and the polymer−solvent thermodynamic interaction parameter τ. Indeed, dielectric spectroscopy appears to be the only way to resolve *both* of these important parameters in a single experiment.

In this paper we report results on four polyelectrolytes, chosen because they have varying amounts of charge and different repulsive interactions with water. Despite these differences, some rather general results emerge that appear to apply to all "hydrophobic" polyelectrolytes. Section II reviews the current understanding of dielectric spectroscopy and combines it with the scaling theory to provide estimates of the parameters f and τ. Section III describes the experiments performed. Section IV presents the interpretation of the measurements based on the equations derived in section II, and section V discusses the significance of these results.

II. Background Theory

Dielectric spectroscopy of aqueous polyelectrolyte solutions without added salt shows three relaxations. At high frequencies ($\nu \cong 17$ GHz) water molecules respond to the applied field[13] and show a maximum in ϵ''. The frequency of this maximum changes as polyelectrolyte is added, suggesting that the polyelectrolyte influences the rotational dynamics of the water molecule, as expected since there is a strong electric field near the polyion. At low frequencies ($\nu < 1$ MHz) there is a relaxation from the polyelectrolyte itself,[14] making dielectric spectroscopy an interesting method for probing the mode structure of the polyelectrolyte chain. However, it is the intermediate frequency relaxation (1 MHz $< \nu <$ 1 GHz) that is the focus of this paper. At intermediate frequencies, where the water molecules easily keep up with the field and the polyion is essentially frozen in space, there is a relaxation due to the mobility of free counterions.

By studying this intermediate relaxation, Ito et al.[12] have shown that information can be obtained about the amount of free counterions in solution. In this section, we review the Ito calculation of the fraction of counterions that are free and show that the effective thermodynamics of polyelectrolyte−water interaction can also be evaluated, in the framework of the scaling theory for polyelectrolyte solutions[5,6] based on the two-state model of counterions.[15−18] The fact that these *two* crucial parameters can be extracted from the same experiment arises because dielectric relaxations are characterized by two features: a frequency and a dielectric increment.

In 1990, Ito et al.[12] suggested that the intermediate relaxation of polyelectrolyte solutions was caused by free counterions polarizing in response to the applied ac field on the scale of the correlation length. Hence, the relaxation time τ_{ion} associated with this intermediate relaxation (at frequency $1/\tau_{\text{ion}}$) is simply the time scale for diffusion of counterions on the scale of the correlation length ξ.

$$\tau_{\text{ion}} = \frac{\xi^2}{6D} \tag{5}$$

D is the diffusion coefficient of the free counterion, which we take to be identical to the diffusion coefficient of that counterion in a monovalent salt solution. Nagamine et al.[19] have recently shown that sulfonated polystyrene with a variety of monovalent counterions having D varying by more than a factor of 10 have $\tau_{\text{ion}} \sim D^{-1}$, consistent with the intermediate relaxation being caused by the motion of free counterions. As discussed above, both the scaling theory and experiment show that $\xi \sim c^{-1/2}N^0$, leading to the expectation that $\tau_{\text{ion}} \sim c^{-1}N^0$ in semidilute solution, as confirmed experimentally for high molecular weight NaPSS[12] in the concentration range 10^{-4} M $< c < 10^{-1}$ M.

The polarizability α_{ion} of the free counterions is determined by their charge e and the polarization distance, assumed by Ito to be the correlation length ξ.

$$\alpha_{\text{ion}} = \frac{e^2\xi^2}{kT} \tag{6}$$

This polarizability determines the second measurable aspect of the intermediate relaxation, its dielectric increment $\Delta\epsilon$, which is the amount that the dielectric constant changes during this relaxation process. Each free counterion contributes polarizability α_{ion}, and the number density of free counterions is fc.

$$\Delta\epsilon = fc\alpha_{\text{ion}} = \frac{fce^2\xi^2}{kT} = fcl_{\text{B}}\xi^2\epsilon_{\text{w}} \tag{7}$$

In the final relation, the definition of the Bjerrum length $l_{\text{B}} \equiv e^2/\epsilon_{\text{w}}kT$ was used. Since $\xi \sim c^{-1/2}N^0$, the dielectric increment should be independent of concentration and chain length in semidilute solution. Ito et al.[12] have demonstrated that $\Delta\epsilon \sim c^0N^0$ for semidilute NaPSS solutions in water with 10^{-4} M $< c < 10^{-1}$ M.

Combining eqs 5 and 7 to eliminate ξ gives the fraction of free counterions.

$$f = \frac{\Delta\epsilon}{6D\tau_{\text{ion}}cl_{\text{B}}\epsilon_{\text{w}}} \tag{8}$$

This relation enables the fraction of free counterions to be determined from measurement of the intermediate frequency dielectric relaxation *alone* for any polyelectrolyte semidilute solution. Combining eqs 1 and 7 to eliminate ξ gives the solvent quality parameter (reduced temperature).

$$\tau = \left(\frac{fb}{l_{\text{B}}}\right)^{1/3}\frac{\Delta\epsilon}{\epsilon_{\text{w}}} \tag{9}$$

Since this relation relies on the correlation length of a polyelectrolyte in a poor solvent for the uncharged monomer (eq 1), it only applies to this case. The measurement of dielectric response in the frequency range of the intermediate relaxation therefore provides a simple means to estimate both the fraction of free counterions and the solvent quality parameter using eqs 8 and 9.

III. Experimental Section

All polyelectrolytes used in this study were dialyzed exhaustively, to a dialyzate conductivity of less than 2 μS/cm prior to use, and care was taken to minimize subsequent contamination with salt. The pH of the solutions was approximately 5.4, consistent with the residual salt concentration of 4×10^{-6} M that is believed to arise from carbonic acid dissociation owing to exposure to CO_2 in air.[20,21] The molecular characteristics of the polymers, determined by size exclusion chromatography, are listed in Table 1. NaPSS is the sodium salt of sulfonated polystyrene, obtained from Scientific Polymer Products (Ontario, NY). NaPAMS (the sodium salt of poly(2-acrylamido-2-methylpropanesulfonate) was synthesized by Wayne Bowman (Kodak) and subsequently fractionated.[22] NaPAMS80-*r*-PA20 is a random copolymer made from 80% 2-acrylamido-2-methylpropanesulfonate and 20% acrylamide. NaPAMS45-*r*-PtBA55 is a random copolymer made from 45% 2-acrylamido-2-methylpropanesulfonate and 55% *tert*-butylacrylamide. NaPSS, NaPAMS, NaPAMS80-*r*-PA20, and NaPAMS45-*r*-PtBA55 solutions at the desired concentrations were prepared with Q-quality water (Millipore) with an electrical conductivity at room temperature of 2 μS/cm or less.

The dielectric spectra of the different polymer aqueous solutions investigated have been measured in the frequency range from 1 MHz to 1.8 GHz by means of a radio-frequency

Table 1. Polyelectrolyte Molecular Characteristics

polymer	M_w	M_w/M_n
NaPSS	1.2×10^6	<1.2
NaPAMS	1.7×10^6	1.3
NaPAMS80-*r*-PA20	1.5×10^6	broad
NaPAMS45-*r*-PtBA55	2.2×10^5	broad

impedance analyzer, Hewlett-Packard model 4291A, at two different temperatures, 20 and 40 °C. The dielectric cell consists of a short section of a coaxial line, with a characteristic impedance of 50 Ω, terminated by a standard APC7 connector and directly connected to the meter.[23]

The real part of the complex permittivity $\epsilon^*(\omega)$ is the permittivity $\epsilon'(\omega)$, and the imaginary part is the dielectric loss $\epsilon''(\omega)$. These are experimentally determined from the complex impedance $Z^*(\omega)$ by solving the bilinear equation that uses three liquids $j = 1, 2, 3$ of known complex dielectric constant as standards.[24]

$$\frac{(\epsilon^* - \epsilon_1^*)(\epsilon_2^* - \epsilon_3^*)}{(\epsilon^* - \epsilon_2^*)(\epsilon_1^* - \epsilon_3^*)} = \frac{(Z^* - Z_1^*)(Z_2^* - Z_3^*)}{(Z^* - Z_2^*)(Z_1^* - Z_3^*)} \qquad (10)$$

Three NaCl solutions of appropriate molarities, with conductivities extending over the range of the samples investigated, were used as standards. Their known complex permittivities ϵ_j^* and measured complex impedances Z_j^* constituted instrument calibration. For each NaCl solution, the complex dielectric constant is written as the sum of a simple Debye relaxation and a conductivity term.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau} + \frac{\sigma_0}{i\omega\epsilon_0} \qquad (11)$$

The parameters ϵ_0, ϵ_∞, τ, and σ_0 have been calculated for the different molarities following Stogryn.[25] Repeated measurements on reference liquids of known conductivity and dielectric constant allow estimation of the overall accuracy, that in the range of conductivities investigated is within 2% on ϵ' and within 5% on ϵ''.

Representative dielectric spectra at selected polymer concentrations are shown in Figure 3. All the polymers investigated show a well-defined dielectric dispersion in the frequency range investigated. The dielectric parameters characterizing this dispersion are the dielectric increment $\Delta\epsilon$, the relaxation time τ_{ion}, and the spread parameter β. They have been determined by a nonlinear least-squares minimization on the basis of a Cole−Cole relaxation function modified by adding a further Debye relaxation to take into account the contribution of the dielectric response of water.

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) + \frac{\sigma_0}{i\omega\epsilon_0} = \epsilon_\infty + \frac{\epsilon_w - \epsilon_\infty}{1 + i\omega\tau_{H_2O}} + \frac{\Delta\epsilon}{1 + (i\omega\tau_{ion})^\beta} + \frac{\sigma_0}{i\omega\epsilon_0} \qquad (12)$$

The high-frequency limit of the permittivity from the intermediate relaxation is the usual dielectric constant of water ϵ_w, while the true high-frequency limit of the permittivity is ϵ_∞. In the limit of very high frequencies, molecules cannot move in response to the field, and only individual atoms can polarize (with dielectric constant ϵ_∞). At lower frequencies, atoms can still polarize, leaving ϵ_∞ as an additive constant (first term). The second term in eq 12 is a Debye relaxation with a dielectric increment $\epsilon_w - \epsilon_\infty$ and relaxation time τ_{H_2O}, describing the orientational relaxation of water molecules. Pure water exhibits a maximum in the dielectric loss dispersion at a frequency of about 17 GHz at room temperature. In the frequency range of our experiments (1 MHz−1.8 GHz) the low-frequency tail of this dispersion produces an increase of the dielectric loss at high frequencies (see Figure 3). The third term is the intermediate relaxation due to diffusion of free counterions within the correlation volume, on time scale τ_{ion} with dielectric increment $\Delta\epsilon$. Empirically, we find that this relaxation is somewhat broader than a simple Debye relaxation, with the spread parameter $\beta = 0.8$ providing a reasonable fit for all data presented here. The fourth term is the contribution from conductivity.

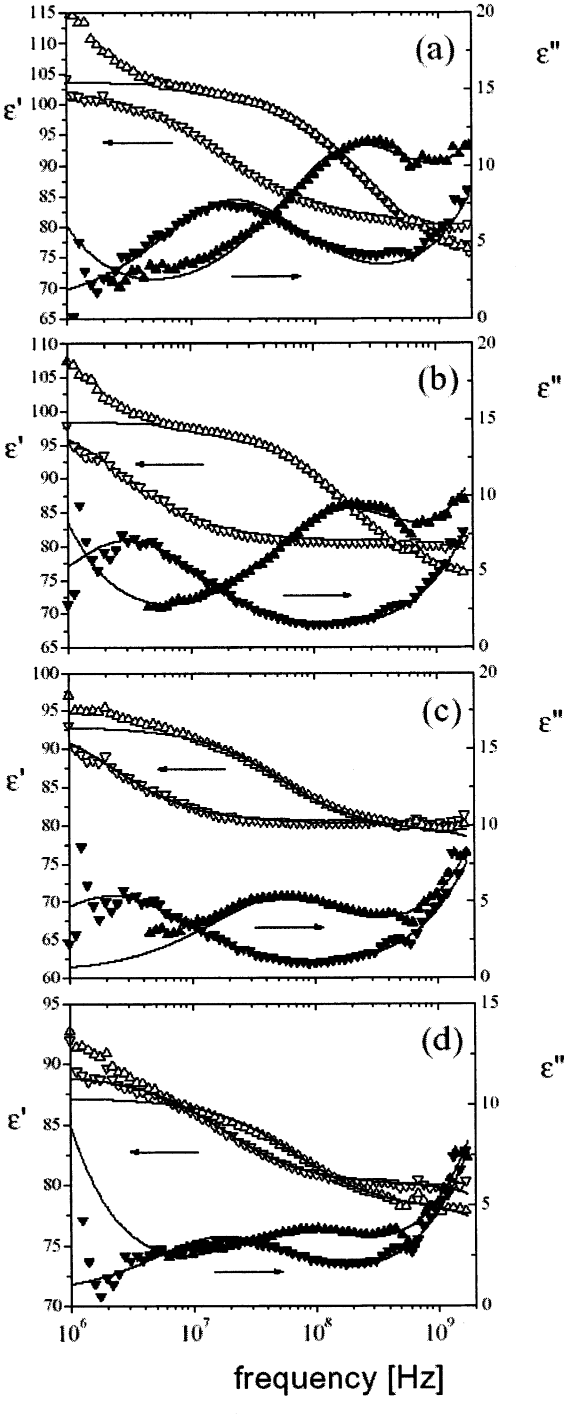

Figure 3. Permittivity ϵ' (open symbols) and dielectric loss ϵ'' (filled symbols) for aqueous solutions of the four polymers investigated at 20 °C as functions of frequency. (a) NaPSS at c = 0.186 M (triangles) and at c = 0.023 M (upside-down triangles); (b) NaPAMS at c = 0.163 M (triangles) and c = 0.0046 M (upside-down triangles); (c) NaPAMS80-*r*-PA20 at c = 0.256 M (triangles) and c = 0.0032 M (upside-down triangles); (d) NaPAMS45-*r*-PtBA55 at c = 0.136 M (triangles) and c = 0.028 M (upside-down triangles). Curves are the model fitting discussed in the text.

The presence of other relaxations at higher and lower frequencies affects the data analysis in some cases. At high

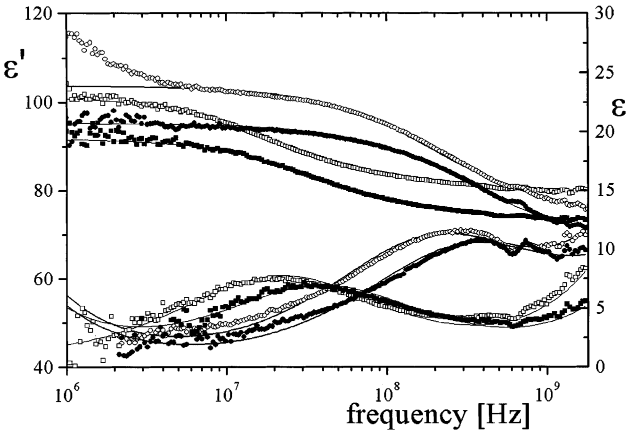

Figure 4. Effect of the temperature changes on the dielectric dispersion of NaPSS at two different concentrations (circles are $c = 0.186$ M and squares are $c = 0.100$ M). Open symbols are at 20 °C, and filled symbols are at 40 °C. Curves are the model fitting discussed in the text. The upper four data sets are the permittivity ϵ' (left axis), and the lower four data sets are the dielectric loss ϵ'' (right axis).

concentrations, the low-frequency wing of the dielectric constant rises, clearly indicating the presence of another relaxation at low frequencies, well below the range investigated in this work. At low concentrations, since the characteristic relaxation time τ_{ion} increases as the polymer concentration decreases, part of the intermediate dispersion is outside the frequency range studied. These effects complicate the resolution of the intermediate dielectric dispersion. Nevertheless, a satisfactory estimation of the parameters of the intermediate dispersion can be obtained using a nonlinear least-squares fitting procedure based on the Levenberg–Marquardt algorithm for complex functions.[13] The method allows the simultaneous fit of the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''(\omega)$. However, since the whole shape of the dielectric loss spectrum $\epsilon''(\omega)$ depends strongly on the low-frequency conductivity σ_0 that is subtracted (see eq 12), a careful fitting procedure is required. Holding the spread parameter fixed at $\beta = 0.8$, the parameters $\Delta\epsilon$, τ_{ion}, ϵ_{w}, and σ_0 are iteratively adjusted until the optimal fit is achieved for each concentration and temperature studied.

Examples of the fits to the data are shown in Figure 4 for two concentrations of NaPSS at 20 and 40 °C. The fits are shown as the solid curves. All solutions investigated show qualitatively similar dielectric dispersions and fits. The upturn in $\epsilon'(\omega)$ at 20 °C for the high-concentration solution at low frequency is caused by another relaxation at lower frequencies and was excluded from the fit.

The results of data fitting are plotted in Figures 5 and 6. Figure 5 shows the dielectric increment $\Delta\epsilon$ with the data at 40 °C normalized to 20 °C in the manner suggested by eq 7. The temperature normalization of eq 7 is clearly reasonable. Ito et al.[12] and Mandel[26] have reported the dielectric increment of NaPSS solutions at lower concentrations, and those data are consistent with the $\Delta\epsilon \cong 20$ observed in Figure 5 for low concentrations of NaPSS. The strongly charged polyions (NaPSS and NaPAMS) have $\Delta\epsilon$ increasing with concentration over the range of concentrations studied. We will see below that this is caused by these chains releasing more of their condensed counterions into the solution. In contrast, the more weakly charged polyelectrolytes (NaPAMS80-*r*-PA20 and NaPAMS45-*r*-PtBA55) have smaller dielectric increments that are independent of concentration, possibly related to the fact that they simply have fewer condensed counterions to release.

The relaxation time τ_{ion} (the reciprocal of the relaxation frequency) is shown in Figure 6 with the data at 40 °C normalized to 20 °C in the manner suggested by eq 5, using the known diffusion coefficients for the Na^+ ion in water (D(293 K) = 1.16×10^{-5} cm^2/s and D(313 K) = 1.90×10^{-5} cm^2/s). This temperature normalization is very good for each of the four polyions, supporting the premise of Ito et al.[12] that the intermediate relaxation corresponds to motion of free counterions. The relaxation time also qualitatively obeys the $\tau_{\text{ion}} \sim c^{-1}$ scaling expected by eq 5, but there are distinct quantitative discrepancies that will lead to concentration dependences of f and τ discussed below.

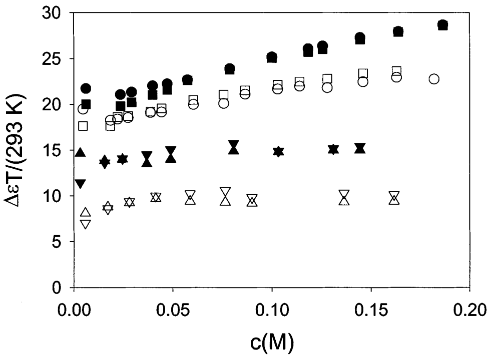

Figure 5. Concentration dependence of the dielectric increment for the intermediate relaxation: filled circles are NaPSS at 20 °C; filled squares are NaPSS at 40 °C; open circles are NaPAMS at 20 °C; open squares are NaPAMS at 40 °C; filled triangles are NaPAMS80-*r*-PA20 at 20 °C; filled upside-down triangles are NaPAMS80-*r*-PA20 at 40 °C; open triangles are NaPAMS45-*r*-PtBA55 at 20 °C; open upside-down triangles are NaPAMS45-*r*-PtBA55 at 40 °C.

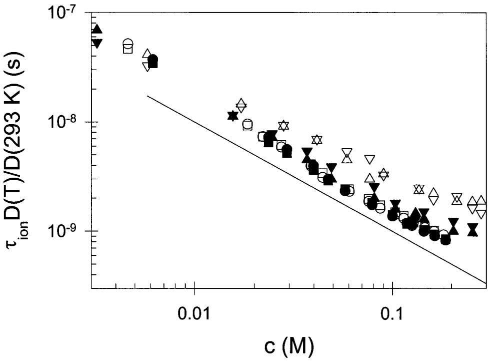

Figure 6. Concentration dependence of the relaxation time for the intermediate relaxation: filled circles are NaPSS at 20 °C; filled squares are NaPSS at 40 °C; open circles are NaPAMS at 20 °C; open squares are NaPAMS at 40 °C; filled triangles are NaPAMS80-*r*-PA20 at 20 °C; filled upside-down triangles are NaPAMS80-*r*-PA20 at 40 °C; open triangles are NaPAMS45-*r*-PtBA55 at 20 °C; open upside-down triangles are NaPAMS45-*r*-PtBA55 at 40 °C. The line shows the slope of −1 expected by eq 5.

IV. Results

Using eq 8, the fraction of monomers with free counterions f is calculated from the dielectric increment $\Delta\epsilon$ and the relaxation time τ_{ion}. Figure 7 shows the concentration dependence of f at two temperatures. Consistent with the osmotic pressure and conductivity (see Figure 2), f is seen to increase as concentration is raised for both highly charged polyelectrolytes (NaPSS and NaPAMS). In contrast, the fraction of charged monomers is independent of concentration for the two less charged polyions (NaPAMS80-*r*-PA20 and NaPAMS45-*r*-PtBA55). For all four polyelectrolytes, the calculations at 20 and 40 °C agree nicely, indicating that f is independent of temperature in this range. Curiously, there are apparent differences between the NaPSS and NaPAMS at high concentrations ($c > 0.05$ M). Furthermore, f seems to *saturate* for both polymers near $c = 0.1$ M, in contrast to the estimations from

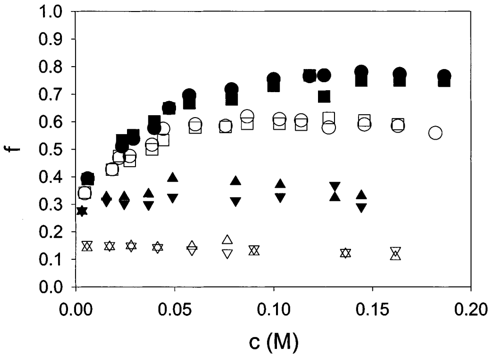

Figure 7. Concentration dependence of the fraction of monomers bearing an effective charge, calculated from the data in Figures 5 and 6 using eq 8: filled circles are NaPSS at 20 °C; filled squares are NaPSS at 40 °C; open circles are NaPAMS at 20 °C; open squares are NaPAMS at 40 °C; filled triangles are NaPAMS80-*r*-PA20 at 20 °C; filled upside-down triangles are NaPAMS80-*r*-PA20 at 40 °C; open triangles are NaPAMS45-*r*-PtBA55 at 20 °C; open upside-down triangles are NaPAMS45-*r*-PtBA55 at 40 °C.

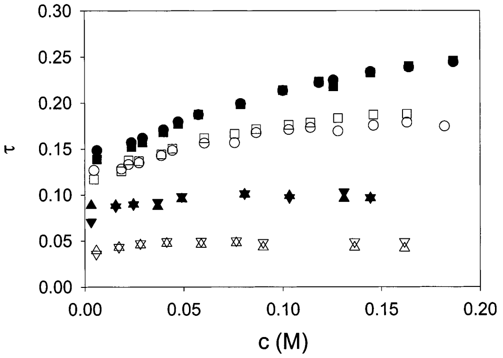

Figure 8. Concentration dependence of the solvent quality parameter, calculated from the data in Figures 5 and 6 using eq 9: filled circles are NaPSS at 20 °C; filled squares are NaPSS at 40 °C; open circles are NaPAMS at 20 °C; open squares are NaPAMS at 40 °C; filled triangles are NaPAMS80-*r*-PA20 at 20 °C; filled upside-down triangles are NaPAMS80-*r*-PA20 at 40 °C; open triangles are NaPAMS45-*r*-PtBA55 at 20 °C; open upside-down triangles are NaPAMS45-*r*-PtBA55 at 40 °C.

osmotic pressure in Figure 2. The saturation values of f calculated from eq 8 differ for the two polyelectrolytes ($f_{\max} \cong 0.75$ for NaPSS and $f_{\max} \cong 0.6$ for NaPAMS). It is not entirely unexpected that f should saturate eventually, as it cannot be larger than unity for these polymers. Our simple analysis could easily miss a prefactor of order unity, but that prefactor should really be the same for the two polymers. Counterion diffusion coefficients have been measured by Ander and Kardan[27] and suggest that the actual diffusion coefficient of Na^+ counterions in our solutions is slightly smaller than the free diffusion coefficient D. The measured counterion diffusion coefficient depends on polyion species and might explain the difference in saturation levels between NaPSS and NaPAMS.

The solvent quality parameter τ, at two temperatures, calculated from eq 9, is plotted as a function of concentration in Figure 8. Once again, the data for all four polyelectrolytes at the two temperatures are very consistent, indicating the expected result that τ only has a very weak temperature dependence (discussed further below). Once again, the strongly charged polyions show a concentration dependence, while the weakly charged polyions have τ independent of concentration. There are again differences between the two strongly charged polyelectrolytes, with water being a somewhat poorer solvent for NaPSS than for NaPAMS. Like the fraction of monomers bearing an effective charge, the solvent quality parameter apparently saturates at high concentrations ($\tau_{\max} \cong 0.25$ for NaPSS and $\tau_{\max} \cong 0.17$ for NaPAMS). These differences in solvent quality for the two polymers are consistent with the known salt effects to determine the θ point (the salt concentration at which intrinsic viscosity scales as the square root of chain length). NaPSS reaches its θ point at 4 M NaCl,[28] whereas NaPAMS still has obvious excluded-volume effects in a saturated NaCl solution.[29,30]

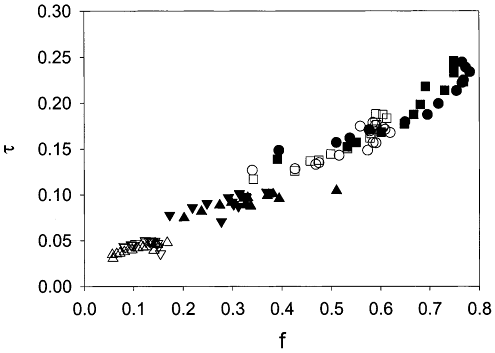

Figure 9. Correlation between the solvent quality parameter and the fraction of monomers bearing an effective charge: filled circles are NaPSS at 20 °C; filled squares are NaPSS at 40 °C; open circles are NaPAMS at 20 °C; open squares are NaPAMS at 40 °C; filled triangles are NaPAMS80-*r*-PA20 at 20 °C; filled upside-down triangles are NaPAMS80-*r*-PA20 at 40 °C; open triangles are NaPAMS45-*r*-PtBA55 at 20 °C; open upside-down triangles are NaPAMS45-*r*-PtBA55 at 40 °C.

The similarities in the concentration dependences of f and τ suggest that there may be some correlation between them. We plot τ as a function of f in Figure 9 for NaPSS, NaPAMS, NaPAMS80-*r*-PA20, and NaPAMS45-*r*-PtBA55 solutions at two temperatures. The more weakly charged polyelectrolytes have both f and τ smaller than the strongly charged polyions (NaPSS and NaPAMS). Furthermore, there is a logical progression in both the fraction of monomers bearing a charge f and the solvent quality parameter τ. As the fraction of monomers having salt groups increases from 0.45 (NaPAMS45-*r*-PtBA55) to 0.8 (NaPAMS80-*r*-PA20) to 1 (NaPAMS), both f and τ steadily increase.

The correlation in Figure 9 strongly suggests that the effective polymer–solvent energetic interaction is *primarily dictated by the effective charge* on the polyelectrolyte chain. This correlation may be related to the fact that water molecules near a bare charge must orient (and thereby lose entropy). The suggestion that the water/polyion interaction is dominated by the loss of entropy of water molecules near the bare charge is perfectly consistent with the insensitivity of τ to temperature. The correct solvent quality parameter of the scaling theory of polyelectrolyte solutions is not the energetic interaction parameter between the uncharged polymer and the solvent, as speculated by Dobrynin et al.[6] This energetic interaction is apparently completely dwarfed by the interaction between water and a bare charge.

V. Discussion

The three methods considered here (osmotic pressure, conductivity, and dielectric spectroscopy) for measuring the effective charge on the polyelectrolyte chain qualitatively agree, but their estimations are quantitatively different. Figure 2a shows that f determined from osmotic pressure and conductivity differ by prefactors of order unity. Such prefactors can arise from simply choosing a slightly different model for describing these measured quantities. For example, the Katchalsky cell model[11] predicts there should be a factor of 2 in eq 2, which is comparable to the factor of 1.8 used to shift the osmotic pressure determined f to overlap with that estimated from conductivity (Figure 2b). The dielectric estimates of f show an increase at high concentrations for the highly charged polyions, but f saturates near $c \approx 0.1$ M, whereas the osmotic pressure data suggest increases in f at higher concentrations (Figure 2).

The underlying reason for these quantitative differences is the approximation of the Oosawa/Manning two-state model for counterions.[15−18] In the two-state model, counterions are imagined to be either completely bound (condensed) on the polyion or completely free. In reality, no counterion exists in either of these states. The Katchalsky cell model predicts that the concentration profile of counterions around the polyion roughly falls off with distance r from the polyion as $1/r^2$ (with a logarithmic correction). Hence, most counterions are quite close to the chain and partially bound. Exactly how many of these partially bound counterions contribute the effect of one truly free counterion depends on the measurement method. Until a better model of counterion distributions is developed, each method will continue to provide a means to estimate the fraction of monomers bearing an effective charge only to within a prefactor of order unity.

Nonetheless, these methods are clearly useful for comparing the charge on different polyelectrolyte chains and also on the same chain at different concentrations. Indeed, the properties of polyelectrolyte chains in solution are well-known to strongly depend on the effective charge, making some measure of the charge on the chain *absolutely crucial* for the field to advance. At present there appear to be three methods available for measuring the effective charge on the chain: conductivity, osmotic pressure, and dielectric spectroscopy. More comparisons of these three measures of effective charge are clearly needed.

Equation 8 suggests that the fraction of monomers bearing an effective charge is proportional to $\Delta\epsilon/(\tau_{\text{ion}}c)$ for a polyelectrolyte solution in a particular solvent at any given temperature. Ito et al.[12] have shown that $\Delta\epsilon/\tau_{\text{ion}}$ is proportional to concentration in the range 10^{-4} M < c < 10^{-1} M for NaPSS (see Figure 6 of ref 12). Thus, over much of the semidilute regime, f is effectively constant. Figure 8 shows that this is no longer true for sufficiently high polyelectrolyte concentrations, qualitatively consistent with Figure 2.

The effective dielectric constant of a polyelectrolyte solution at lower frequencies ($\nu \ll 1/\tau_{\text{ion}}$) is $\epsilon_w + \Delta\epsilon$. Thirty years ago, Oosawa recognized that the effective dielectric constant of polyelectrolyte solutions was larger than that of pure water and increased with polyelectrolyte concentration (see Figure 15 of ref 17). He suggested that the larger dielectric constant was due to the polarizability of the condensed counterions on the polyion. Our data analysis here suggests that this interpretation is not quite correct. The effective dielectric constant ($\epsilon_w + \Delta\epsilon$) is controlled by changes in both terms. At 20 °C, for example, the dielectric constant of water actually decreases weakly from $\epsilon_w \cong 80$ for pure water (and for $c \lesssim 0.5$ M) to $\epsilon_w \cong 74$ for $c \cong 0.2$ M for NaPSS and NaPAMS solutions. This decrease arises quite naturally, since as polyelectrolyte concentration increases, more of the water finds itself close to the strong field of the polyion and hence is less able to respond to an external field. As Figure 5 shows for NaPSS and NaPAMS solutions, $\Delta\epsilon$ increases much more than ϵ_w decreases in the same concentration range. This makes the effective dielectric constant of the polyelectrolyte solution ($\epsilon_w + \Delta\epsilon$) increase with polyelectrolyte concentration. The increase apparently comes from the release of condensed counterions into the solution ($\Delta\epsilon$) that is partially offset by a reduction in the polarizability of water (ϵ_w).

VI. Conclusions

We have demonstrated a simple means of determining the effective charge and solvent interaction parameter for polyelectrolyte solutions from dielectric spectroscopy measurements. Since the charge on the chain and the solvent quality parameter both change with concentration, the dielectric measurement may provide the key to developing an understanding of polyelectrolyte solutions. A superb example of this is the fortuitous agreement of the concentration dependence of the correlation length of NaPSS and NaPAMS solutions with the scaling predictions. Both the charge on the chain and the solvent quality parameter increase as concentration increases, and their effects on the correlation length happen to cancel each other.

There is a very strong correlation between the fraction of monomers bearing an effective charge and the solvent quality parameter. This correlation, shown in Figure 9, exists without regard to the chemical nature of the polyion chain, which strongly suggests that the solvent interaction parameter is dominated by the interactions of water with a bare charge. This dominance needs to be verified with other polyelectrolytes but stands to markedly change the way we think about polyelectrolyte solutions.

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