

Electrical Conductivity of Polyelectrolyte Solutions in the Semidilute and Concentrated Regime: The Role of Counterion Condensation

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The d.c. electrical conductivity of polyacrylate sodium salt and poly(acrylic acid) aqueous solutions of different molecular weights from 2 to 200 kD has been investigated in a wide range of polymer concentration, covering both the semidilute (unentangled and entangled) and concentrated regimes. The data have been analyzed on the basis of a modified version of the Manning theory of counterion condensation, to cover the semidilute regime, taking into account scaling arguments recently proposed by Dobrynin et al. (*Macromolecules* **1995**, *28*, 1859). This analysis, on the basis of the conductivity model we have adopted, provides evidence for a fraction of free counterions that increases with the polymer concentration until the semidilute-concentrated crossover concentration is reached, suggesting that, in the concentration range investigated, the effective charge on the polyion is dependent on the polymer concentration. Moreover, at the higher concentrations investigated, our data suggest that a regime is attained where electrostatic blobs overlap, strongly affecting the electrical transport properties of the solution and causing a progressive reduction of the free counterion concentration.

1. Introduction

Polyelectrolytes are macromolecules with many ionizable groups which, in aqueous solution and under appropriate conditions, dissociate, leaving ionized charged groups on the polyion backbone and counterions in the bulk solution.^{1–6} Owing to a fine interplay between electrostatic interactions of counterions with the polymer chain and the entropic contribution deriving from the bulk solution, aqueous polyelectrolyte solutions display a peculiar behavior, different from that of neutral polymer solutions and that of the simple electrolytes.

Extensive experimental data are available in the literature^{7–11} showing these differences in a variety of physicochemical parameters. At present, however, there are no theories which explain the major features of the dynamics of aqueous polyelectrolyte systems, in particular the general dependence of transport and colligative properties on the polymer concentration, solvent quality, and strength of electrostatic interactions.

Most of the existing theories are based on the assumptions that the effective charge on the polyion chain and the solvent quality parameter do not change with the polymer concentration. These assumptions, although apparently reasonable, could represent a serious limitation in the development of a comprehensive theory of polyelectrolyte aqueous solutions in the whole concentration regime.

Although the ionic interactions between the polyion and the counterions, which definitely characterize the polyelectrolyte character of the system, may be investigated by means of various coefficients, the electrical conductivity represents a significant parameter because it takes into account the movement of any charged entity present in the aqueous system (polyion, counterions, and ions deriving from added salt) under the influence of an external electric field.

Although the d.c. electrical conductivity behavior of a highly charged polyelectrolyte solution in the limit of very high dilution has been explained theoretically on the basis of the Manning counterion condensation theory,^{12–14} a complete description in other concentration regimes, particularly in the semidilute unentangled, semidilute entangled, and, moreover, concentrated regimes, has not been yet developed, although various attempts have been made to include possible effects of the chain conformation.^{15,16}

The scaling concepts applied to polyelectrolyte solutions^{17–19} have been successfully proposed many years ago, and more recently, Dobrynin et al.²⁰ give a description of the charged polymer conformation in different concentration regimes, covering both the dilute and semidilute region. On the basis of this scaling treatment, we have recently proposed²¹ a modified version of the Manning counterion condensation model to take into account the different chain conformations which dominate in the low-concentration limit from those which become

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prominent with increasing concentration (semidilute and concentrated regimes). We found scaling predictions in good agreement with experimental data of electrical conductivity on dilute and semidilute poly(L-lysine) hydrobromure aqueous solutions of different molecular weights from 4 to 167 kD.

In this work, we have further analyzed the electrical conductivity (in the low-frequency limit) of simple polyelectrolyte aqueous solutions (sodium polyacrylate and poly(acrylic acid), in this case) in a more extended concentration range, covering the dilute-semidilute and semidilute-concentrated regimes.

Because the main contribution to the electrical conductivity (and to other colligative properties) of the polyelectrolyte solutions comes from the counterion condensation associated with the conformational changes of the polymer chain, scaling theory should be a good candidate to predict the observed conductometric behavior of polyelectrolyte solutions in the semidilute regime. Our results suggest that the effective charge on the polyion chain, incorporating any effect of counterion condensation, depends on the polymer concentration, resulting in a fraction of free counterions that reaches a maximum at the crossover between semidilute and concentrated regimes and then decreases as the concentration is further increased.

The relevance of this approach in the description of the conductometric behavior of polyelectrolyte solutions is briefly discussed.

2. Experimental Section

2.1. Materials. Six sodium polyacrylate samples, $[-CH_2CH-(CO_2Na)-]_n$, with nominal molecular weights of 2.1, 5.1, 20, 60, 140, and 225 kD, respectively, and two poly(acrylic acid) samples with nominal molecular weights of 5.0 and 50 kD were purchased from Polysciences Inc. (Warrington, PA) as 20 or 25 wt % solutions in water. The samples were used as received, without any further purification. All of the solutions investigated were prepared at the desired polymer concentration in the range from 10^{-2} to 10 monomol/L with deionized Q-quality water (Millipore), whose electrical conductivity was less than $1-2 \times 10^{-6}$ mho/cm at room temperature.

2.2. Dielectric and Conductivity Measurements. The dielectric and conductivity properties of sodium polyacrylate aqueous solutions have been measured by means of frequency-domain dielectric spectroscopy, in the frequency range from 1 MHz to 1.8 GHz, using a Hewlett-Packard Impedance Analyzer model 4291A. All measurements have been carried out at the temperature of 20.0 °C within 0.1 °C.

The input impedance $Z^*(\omega)$ of the dielectric cell has been converted to the complex dielectric constant $\epsilon^*(\omega)$ of the sample by solving the bilinear equation^{22,23}

$$\frac{[\epsilon^*(\omega) - \epsilon_1^*(\omega)][\epsilon_2^*(\omega) - \epsilon_3^*(\omega)]}{[\epsilon^*(\omega) - \epsilon_2^*(\omega)][\epsilon_1^*(\omega) - \epsilon_3^*(\omega)]} = \frac{[Z^*(\omega) - Z_1^*(\omega)][Z_2^*(\omega) - Z_3^*(\omega)]}{[Z^*(\omega) - Z_2^*(\omega)][Z_1^*(\omega) - Z_3^*(\omega)]} \quad (1)$$

where $\epsilon_i^*(\omega)$ and $Z_i^*(\omega)$ ($i = 1, 2$, or 3) are the complex dielectric constants and the measured impedances of three different liquids used as standard for the setup calibration. The overall accuracy, in the range of conductivities investigated in the whole frequency range, is within 2% on $\epsilon'(\omega)$ and within 5% on $\epsilon''(\omega)$.

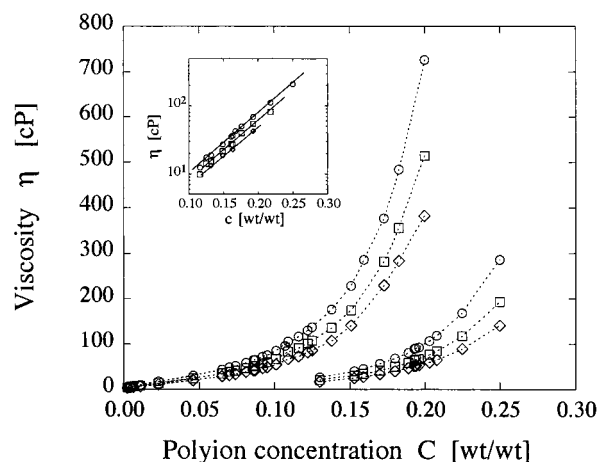


Figure 1. Viscosity of sodium polyacrylate aqueous solutions at two different molecular weights, 140 and 225 kD, at three different temperatures: (○) $T = 20$ °C; (□) $T = 30$ °C; (◇) $T = 40$ °C. The dotted lines serve to guide the eye, only. The inset shows the viscosity of poly(acrylic acid) aqueous solutions at the same three temperatures, for a molecular weight of 50 kD.

The complex dielectric constant $\epsilon^*(\omega)$ is related to the dielectric parameters of the system through the relation

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon'(\omega) - i\left(\epsilon''_{\text{diel}}(\omega) + \frac{\sigma_0}{\epsilon_0\omega}\right) \quad (2)$$

where $\epsilon'(\omega)$, $\epsilon''_{\text{diel}}(\omega)$, and σ_0 are the permittivity, the dielectric loss, and the d.c. electrical conductivity, respectively.

The present paper is concerned mainly with the conductivity properties of the polymer solutions investigated, with their dielectric properties being discussed and analyzed in detail in a forthcoming paper.²⁴

2.3. Viscosity Measurements. The viscosity measurements of sodium polyacrylate aqueous solutions were carried out at three temperatures (20, 30, and 40 °C) at different values of the shear rate in the range $0.1-10^3 \text{ s}^{-1}$, using a Haake RheoStress RS 150 rheometer.

We investigated three different molecular weights, using a coaxial cylinder geometry and two different sensors, model Z20 DIN for samples of viscosity larger than 20–30 cP and model Z40 DIN for samples of lower viscosity. The measuring cell was modified by placing a guard plastic cone to minimize sample evaporation. The temperature was controlled by means of a Haake K35 water bath equipped with a D50 unit temperature control within 0.1 °C. For all of the molecular weights investigated, samples at the higher concentrations show a marked shear thinning effect. We report here only the Newtonian viscosity values observed for all of the samples, at least, over one decade of shear rate independent apparent viscosity. Figure 1 shows the viscosity behavior of two selected molecular weight polymer solutions (140 and 225 kD, respectively) as a function of polymer concentration, at three different temperatures.

2.4. Polyelectrolyte Behavior. The pH values of the solutions, for all of the molecular weights investigated show a continuous moderate decrease as the polymer concentration is increased, varying from about pH = 9.0 at $C = 0.01 \text{ g/mL}$ to about pH = 8.00 at $C = 0.40 \text{ g/mL}$, at the highest concentration investigated. At these pH values, the carboxylic groups dissociate, the polymer gains a number of negative charges producing positive counterions, and consequently the polymer behaves as a polyelectrolyte. The number of dissociated groups

on the polyion depends on the addition of sodium hydroxide to the poly(acrylic acid) and is reflected by the pH value of the solution.

The polyelectrolyte chain has a nominal charged group per monomer with a monomer projection equal to $b = 2.52 \text{ \AA}$.²⁵ In aqueous solution, the charge density parameter $\xi = l_B/b = e^2/(\epsilon_w k_B T b) = 2.83$ is larger than the critical value $\xi_c = 1$ and, according to the Manning theory,^{12,13} counterion condensation will occur. Because in the whole semidilute regime the value of pH is approximately constant to the value pH = 8.8–8.9, no correction was made on the “structural” charge density in the polymer chain. Here, l_B is the Bjerrum length (about 7.2 Å in water at 25 °C) which corresponds to a distance where the electrostatic and thermal energies balance. ϵ_w is the dielectric constant of the aqueous phase, and $k_B T$ is the thermal energy.

3. Theoretical Background

3.1. Electrical Conductivity of a Polyelectrolyte Solution.

The polyelectrolyte solution is modeled as a random collection of polymer chains of contour length l containing N monomers and bearing an electric charge $q_l = eNf$. Note that f is the inverse of the number of monomers between effective charge and consequently takes into account the effect of counterion condensation. The electrical conductivity can be written, on the basis of a simple additive rule, as

$$\sigma = \sum_i (|z_i|e)n_i u_i \quad (3)$$

where each charged entity (polyions, counterions and eventually ions derived from added salt) contributes through its concentration n_i , its charge $z_i e$ and its mobility u_i . In the absence of added salt and in the presence of counterion condensation, eq 3 reads

$$\sigma = c \frac{b}{l_B} (\lambda_1 + \lambda_p) \quad (4)$$

where c (in monomol per unit volume) is the polyion concentration and λ_1 and λ_p are the equivalent ionic conductance of counterions and polyions, respectively.

3.1.1. The Manning Model on the Basis of the Scaling Approach. From an electrical point of view, the scaling approach describes a polyelectrolyte solution with no added salt identifying three scale lengths, according to the conformational features assumed by the polyion.

In the dilute regime, the chain is represented by an extended rodlike configuration of N_D electrostatic blobs of size D . Each of them, containing g_e monomers, bears a charge $q_D = f e g_e$, with f the fraction of ionized charged groups on the polyion chain (and consequently, the fraction of free counterions).

In the semidilute regime, the polyion chain is represented as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers and bearing an electric charge $q_\xi = e f g$. Because of the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of electrostatic blobs.

At higher concentrations, significant overlap of neighboring chains occurs, and this strongly affects the chain motion (semidilute entangled regime). At even higher concentrations, electrostatic blobs begin to overlap, and owing to the increase of electrostatic, excluded volume, and hydrodynamic interactions, scaling arguments²⁶ suggest a polyelectrolyte behavior similar to that of a neutral solution.

Each of these three regimes is associated with a characteristic length scale that identifies a characteristic polyion concentration,

i.e., a concentration c^* , at which the distance between chains equals their extended length, a concentration c_e where the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length (i.e., Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for the strand of N/g beads of size ξ_0), and finally a concentration c_D , where electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size. The polymer solution behaves as a dilute solution for $c < c^*$, as a unentangled-semidilute solution for $c^* < c < c_e$, as a entangled-semidilute solution for $c_e < c < c_D$, and finally as a concentrated solution for $c > c_D$.

In a recent paper,²¹ we have described the electrical conductivity of a polyelectrolyte solution on the basis of an extension of the Manning model of counterion concentration, which is valid only at infinite dilution. To remove this limitation, we have calculated the polyion mobility u_p in either the dilute or semidilute regime, on the basis of the scaling theory proposed by Dobrynin et al.²⁰ The main differences with the Manning model can be summarized as follows: (i) the electrostatic blob, instead of the monomer, is the elementary unit that contribute to the overall friction coefficient, (ii) the effect of the polymer concentration on the overall configuration of the chain is taken into account through the concentration dependence of the correlation length, and (iii) the fraction of free counterions and the solvent quality are not assumed a priori independent of the polyion concentration, but conversely, the solvent quality could change with the concentration, influencing both the local configuration of the chain (the size of the electrostatic blobs) and the polyion-counterion interactions (the fraction of free counterions).

On the basis of these assumptions, the polyion mobility u_p can be written (in the usual units) as

$$u_p = \frac{1}{300} \frac{\frac{D_1^u}{D_1^0} q_l}{\left(1 - \frac{D_1^u}{D_1^0} \frac{q_l}{u_c^0} + \frac{3\pi\eta N_D D}{\ln(N_D)}\right)} \quad (5)$$

in the dilute regime ($c < c^*$) and

$$u_p = \frac{1}{300} \frac{\frac{D_1^u}{D_1^0} q_l}{\left(1 - \frac{D_1^u}{D_1^0} \frac{q_l}{u_c^0} + \frac{3\pi\eta N_\xi \xi_0}{\left(1 + \frac{8}{\sqrt{6\pi}} \frac{\sqrt{N_\xi}}{\ln(g/g_e)}\right) \ln(g/g_e)}\right)} \quad (6)$$

in the semidilute regime ($c > c^*$), where D_1^u/D_1^0 is the ratio of the self-diffusion coefficients of free counterions in the polyelectrolyte solution in the presence and in the absence of the polyion, respectively, and u_c^0 is the infinite dilution counterion mobility. According to Dobrynin et al.,²⁰ the following scaling relationships hold

$$D \approx b(l_B/b)^{3/7} f^{-6/7} \quad (7)$$

$$N_D D \approx N b (l_B/b)^{2/7} f^{4/7} \quad (8)$$

in the dilute regime ($c < c^*$) and

$$(g/g_e) \approx b^{-3/2} (l_B/b)^{2/7} f^{4/7} c^{-1/2} \quad (9)$$

$$N_{\xi} \approx Nc^{1/2}b^{3/2}(l_B/b)^{3/7}f^{6/7} \quad (10)$$

$$N_{\xi}\xi_0 \approx Nb(l_B/b)^{2/7}f^{4/7} \quad (11)$$

in the semidilute regime ($c > c^*$), respectively. It must be noted that both $N_D D$ and $N_{\xi}\xi_0$ equal the chain size L . In these scaling relationships, we have considered the aqueous phase as a “good” solvent; that is, we have assumed the temperature $T \gg \theta$, where θ is the temperature at which the net excluded volume for the uncharged monomer is zero. Consequently, the conductivity of the polyelectrolyte solution depends on a single parameter, i.e., the fraction f of free counterions. In the above scaling relationships (eqs 7–11), we have assumed the prefactors of the order of unity, as routinely done with scaling arguments. However, to verify how this assumption could affect our final results, for example in the case of dilute regime, we have evaluated the fraction f of free counterions, assuming the prefactors estimated from reasonable values of both the electrostatic blob size D and the number N_D of blobs per each chain. In this case, differences are confined within few percent. Similar behavior is expected for the semidilute regime.

3.1.2. A Further Scaling Model. On the basis of the same scaling theory but with a slightly different approach, another simple model that describes the electrical conductivity of polyelectrolyte solutions in the absence of added salt has been recently proposed.²⁷ These two models differ mainly in the way of taking into account the so-called “asymmetry effect”, due to the fact that, when viewed from the polyion, the cloud of surrounding counterions is distorted, diminishing the effective field that acts on the polyion itself. Nevertheless this difference, the two above models give quite similar results in the semidilute regime, where the counterion cloud and the coherently moving part of the polyion are of the same size and the asymmetry effect is reduced. For sake of completeness, we will report here the main features of this model. As above, inside each correlation blob of length ξ_0 , the polyion is modeled as an extended rodlike chain of electrostatic blobs of size D . The polyion mobility can be written as

$$u_p = \frac{1}{300} \frac{q_{\xi} \ln(\xi_0/D)}{3\pi\eta\xi_0} \quad (12)$$

The simple additivity of contributions from polyions and counterions results in the following expression for the electrical conductivity²⁷

$$\sigma = fc(ze)(u_c + u_p) = \frac{fc}{\mathcal{N}} \left(\lambda_c + \frac{F}{300} \frac{q_{\xi} \ln(\xi_0/D)}{3\pi\eta\xi_0} \right) \quad (13)$$

It must be noted that, if the field asymmetry effect is negligible, eq 6 reduces to

$$u_p = \frac{1}{300} \frac{D_1''}{D_1^0} \frac{q_1 \ln(g/g_e)}{3\pi\eta N_{\xi}\xi_0} \left(1 + \frac{8}{\sqrt{6\pi}} \frac{\sqrt{N_{\xi}}}{\ln(g/g_e)} \right) \quad (14)$$

that, under the conditions $q_1 = Nef$, $N/N_{\xi} = g$ and $\xi_0/D = g/g_e$, becomes very similar to eq 12. If the further assumptions hold $D_1''/D_1^0 \approx 1$ and

$$\frac{8}{\sqrt{6\pi}} \frac{\sqrt{N_{\xi}}}{\ln(g/g_e)} \ll 1 \quad (15)$$

eqs 2 and 14 become identical. It follows that this model can

be considered as a simplified version of the modified Manning model when the asymmetry field effect is negligible and the number of correlation blobs for each chain is sufficiently small. Finally, it is noteworthy to observe that the two models, obtained following a different derivation, but based on a common scaling picture of the polyelectrolyte solution, give a very similar expression for the polyion mobility.

According to the scaling properties,²⁰ the following relationships hold

$$q_{\xi} \approx ec^{-1/2}b^{-3/2}(b/l_B)^{3/7}f^{-1/7} \quad (16)$$

$$\xi_0 \approx f^{-2/7}l_B^{-1/7}b^{-5/14}c^{-1/2} \quad (17)$$

$$\xi_0/D \approx c^{-1/2}f^{4/7}(b/l_B)^{-2/7}b^{-3/2} \quad (18)$$

and the mobility u_p becomes

$$u_p = \frac{1}{300} \frac{eb^{-1}(l_B/b)^{-2/7}f^{3/7}}{3\pi\eta} \ln(b^{-3/2}(l_B/b)^{2/7}f^{4/7}c^{-1/2}) \quad (19)$$

Finally, eq 13, expressed in the usual standard units, reads

$$\sigma = \frac{fc}{\mathcal{N}} \left(\lambda_c + \frac{F}{300} \frac{ef^{3/7}b^{-5/7}l_B^{-2/7}}{3\pi\eta} \ln(c^{-1/2}f^{4/7}(b/l_B)^{-2/7}b^{-3/2}) \right) \quad (20)$$

and also in this case the model has a single free parameter, the fraction f of uncondensed counterions.

As can be seen, both of the two above model have a single free parameter, the fraction f of free counterions that defines the fraction of the effectively ionized groups along the polyion chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to a polyelectrolyte solution in the high dilute regime and predicts a fraction of condensed counterions independent of the polymer concentration given by the value of the charge-density parameter $\xi = l_B/b$, eqs 6 and 19 can be applied to more concentrated systems, up to the concentration c_D .

4. Results and Discussion

The low-frequency electrical conductivity behavior of sodium polyacrylate and poly(acrylic acid) aqueous solutions as a function of the polymer concentration, for different molecular weights, is shown in Figures 2 and 3, respectively.

For all of the samples investigated, the conductivity increases with the polymer content up to a concentration of about 1.2–2 monomol/L, and then, after a wide plateau, it decreases up to 4.5 monomol/L (the highest concentration studied). The data, plotted in a log–log scale (insets of Figures 2 and 3) show a marked power-law behavior, with deviations being evident both at low and high concentrations. These deviations, slightly depending on the molecular weight and particularly marked at concentrations of about 1.5–2 monomol/L, define the transition from different concentration regimes.

The data have been analyzed on the basis of the two above stated models (eqs 12 and 19), using f as an adjustable parameter.

To compare the model predictions with the experimental results, we must define the concentration regimes the system experiences. The overlap concentration c^* , above which the chain overlap, is defined as the concentration for which the distance $R_M \approx (N/c)^{1/3}$ between two polymer chains equals the length $L = Nb/B$, i.e.

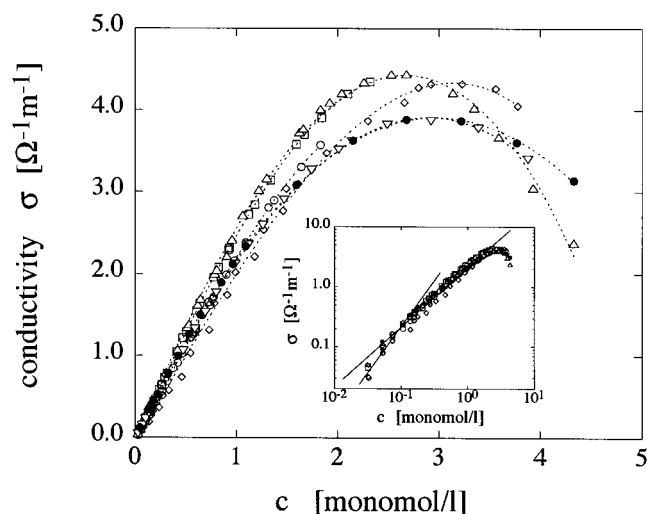


Figure 2. Electrical conductivity of sodium polyacrylate aqueous solutions as a function of the polymer concentration at the temperature of 20 °C, for different molecular weights: (○) 225 kD; (□) 140 kD; (◇) 60 kD; (Δ) 20 kD; (▽) 5.1 kD; (●) 2.1 kD. The dotted lines serve to guide the eye, only. The inset shows the same data in a log–log plot. Deviations from a straight line evidence different concentration regimes.

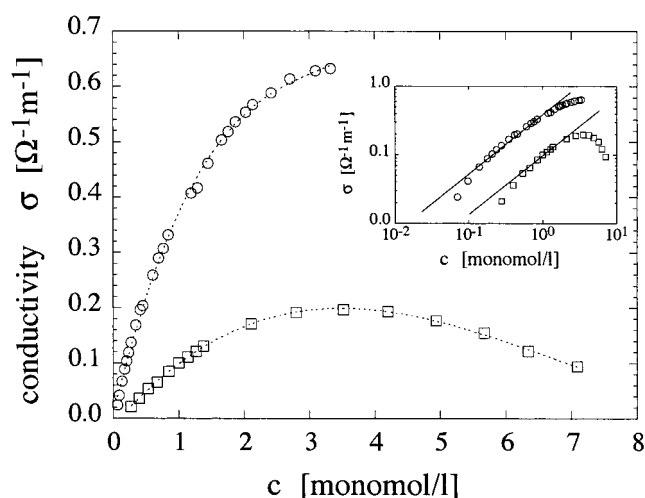


Figure 3. Electrical conductivity of sodium polyacrylate aqueous solutions as a function of the polymer concentration at the temperature of 20 °C, for two different molecular weights: (□) 5 kD; (○) 50 kD. The dotted lines serve to guide the eye, only. The inset shows the same data in a log–log plot. Deviations from a straight line evidence different concentration regimes.

$$c^* = \frac{1}{N^2} \left(\frac{B}{b} \right)^3 \quad (21)$$

where the parameter B is defined as the ratio of the chain contour length $l = Nb$ and the fully extended chain length of electrostatic blobs

$$B \equiv \frac{Nb}{N_D D} \approx \left(\frac{b}{\sqrt{e} l_B} \right)^{2/7} \quad (22)$$

The concentration c_e , at which entanglement effects begin, is defined as

$$c_e \approx \frac{nN}{R^3} \approx n^4 c^* \quad (23)$$

where the “universal” number n was estimated to be $n \approx$

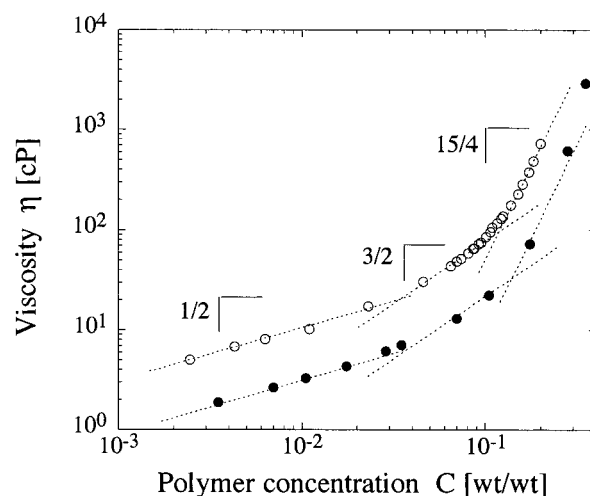


Figure 4. Viscosity of sodium polyacrylate aqueous solutions as a function of polymer concentration for two different molecular weights: (○) 225 kD; (●) 60 kD. The dotted lines represent the expected power-law behavior according to the concentration regime, where the exponents are 1/2, 3/2, and 15/4 for semidilute unentangled, semidilute entangled, and concentrated regimes, respectively.

5–10.²⁰ Finally, the concentration c_D , at which the electrostatic blobs begin to overlap, is given by

$$c_D \approx \frac{g_e}{D^3} \quad (24)$$

For example, in the case of the sample with molecular weight 225 kD, assuming a value of $B = 3$ and $n = 5$, we obtain an overlap concentration c^* of about $c^* \approx 5 \cdot 10^{-4}$ monomol/L and an entanglement concentration c_e of about $c_e \approx 0.4$ monomol/L. Finally, if we assume a number of monomer inside each electrostatic blob equals to $g_e \approx 45$ and a blob size of $D \approx 38$ Å, we may estimate a concentrated regime for concentrations higher than $c_D \approx 1.3$ monomol/L.

Experimental evidences to these values that separate the different polyion concentration regimes, comes from the viscosity measurements. Figure 4 shows a typical behavior of the Newtonian viscosity for samples of 225 and 60 kD at the temperature of 20 °C. As can be seen, when the data are shown in a log–log plot, three different regimes are clearly evidenced with value of the scaling exponents that compares reasonably well with the values expected for solutions in the absence of added salt for semidilute-unentangled regime, $\eta \approx c^{1/2}$, for the semidilute-entangled regime, $\eta \approx c^{3/2}$, and for the concentrated regime, $\eta \approx c^{15/4}$.²⁸ The crossover concentrations between the different regimes derived from the viscosity measurements are in good agreement with the above quoted values, and these indications give support to the analysis of the conductometric behavior on the basis of solutions in semidilute and concentrated regime, with the dilute regime being well below the lowest concentration investigated.

Both of the conductometric models we have discussed depend on a free parameter, the fraction f of free counterions. Figures 5 and 6 show this parameter f as a function of polymer concentration, derived from eqs 6 and 19 valid in the semidilute regime, respectively, on the basis of a nonlinear least-squares fitting procedure. For all of the molecular weights investigated, f shows a peculiar behavior evidencing a marked increase in the semidilute-unentangled regime, an approximately constant value in the semidilute-entangled regime, and a pronounced decrease at concentrations larger than the concentration c_D . An

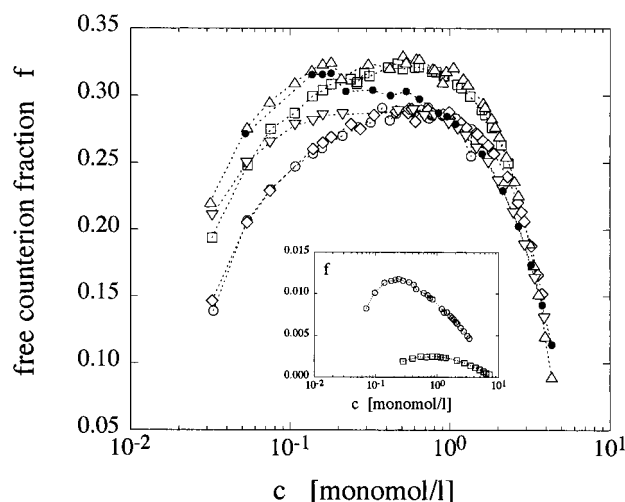


Figure 5. Fraction f of free counterions in sodium polyacrylate aqueous solutions as a function of polymer concentration deduced from eqs 4 and 6, for the different molecular weights investigated: (○) 225 kD; (□) 140 kD; (◇) 60 kD; (△) 20 kD; (▽) 5.1 kD; (●) 2.1 kD. The dotted lines serve to guide the eye, only. The inset shows the fraction f of free counterions in poly(acrylic acid) aqueous solutions, deduced from eqs 4 and 6, for two different molecular weights: (□) 5 kD; (○) 50 kD.

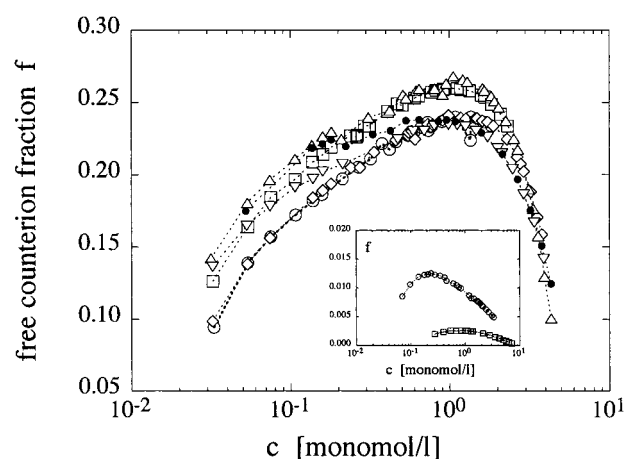


Figure 6. Fraction f of free counterions in sodium polyacrylate aqueous solutions as a function of polymer concentration deduced from eq 20 for the different molecular weights investigated: (○) 225 kD; (□) 140 kD; (◇) 60 kD; (△) 20 kD; (▽) 5.1 kD; (●) 2.1 kD. The dotted lines serve to guide the eye, only. The inset shows the fraction f of free counterions in poly(acrylic acid) aqueous solutions, deduced from eqs 4 and 6, for two different molecular weights: (□) 5 kD; (○) 50 kD.

invariance of the correlation length ξ_0 , related to a renormalization of the charge fraction in the sense of the Manning model, has been recently observed in the semidilute regime of a linear hydrophilic polyelectrolyte by Essafi et al.²⁹ on the basis of small-angle neutron and X-ray scattering measurements. This finding means a fraction f of free counterions independent of the polymer concentration (in the semidilute entangled region) as that observed in the present work.

Although the data do not allow us to clearly evidence a molecular weight dependence, the f decrease begins for all of the polymers studied approximately at the same concentration c_D . This finding gives further support to the assumption that this concentration corresponds to the overlapping of the electrostatic blobs, whose sizes in the scaling model are independent of the molecular weight.

Moreover, it is noteworthy that the concentration dependence of f derived either from eq 6 or eq 19 is qualitatively similar,

suggesting that the results can be considered as “model” independent.

The observed behavior of the fraction f in the overall semidilute regime and consequently of the counterion condensation on the polymer chain can be attributed to its strong correlation with the similar behavior of the solvent quality parameter, suggesting that the effective polymer–solvent energetic interaction is governed by the effective charge on the polyelectrolyte chain. At higher concentrations, when the electrostatic blob overlapping occurs, the counterion condensation level increases again, pointing out a significant role of the loss of entropy of the solvent because of the ordering of water molecules around a bare charge.

Finally, we have recently suggested³⁰ that a possible evaluation of the fraction of free counterions derives from the dielectric dispersion generally occurring in these polyelectrolyte systems measured by means of radiowave dielectric spectroscopy methods. In the frequency range (approximately from 1 MHz to 1 GHz) intermediate between that where the polarization due to the whole polyion dominates and that where the relaxation of the pure water occurs, a well-defined dielectric contribution appears, associated with the mobility of free counterions. In the semidilute regime, this dielectric response is characterized by a counterion diffusion on a scale of the correlation length ξ_0 , resulting in a relaxation frequency $\nu_0 \approx D_1^0/\xi_0^2$ and a dielectric increment $\Delta\epsilon \approx f c \xi_0^2 l_B \epsilon_w$.³¹

Combining the two above relationships to eliminate the correlation length ξ_0 , (eq 17), gives

$$f \approx \frac{\nu_0 \Delta\epsilon}{D_1^0 c l_B \epsilon_w} \quad (25)$$

where $\Delta\epsilon$ and ν_0 are the measured parameters (the dielectric increment and the relaxation frequency) of the observed intermediate dispersion and $D_1^0 \approx u_c^0$ the free diffusion coefficient of counterions.

This relationship, explicitly derived as a function of the concentration c , offers the possibility to evaluate the fraction f from the dielectric parameters only, without any contribution from the conductivity measurements. It is noteworthy that, also in this case, f presents qualitatively the same dependence shown in Figure 5. These aspects will be considered in detail in a forthcoming paper.²⁴

In the present case, the dielectric relaxation parameters $\Delta\epsilon$ and ν_0 and their dependence on the concentration c furnish support to the above analysis based, for the particular polymer considered, on the hypothesis of a “good” solvent. In this case, substitution of eqs 17 and 25 into the scaling relationship $\nu_0 \approx D_1^0/\xi_0^2$ yields

$$\frac{\Delta\epsilon^{4/3}}{\nu_0} \approx c^{-1} \quad (26)$$

As can be seen in Figure 7, this power-law dependence is strictly verified for all of the molecular weights investigated. The possibility of evaluating the role of the solvent quality parameter from dielectric relaxation measurements will be discussed in detail elsewhere.²⁴

A final comment is in order. Both of the two above stated models do not apply in the concentrated regime ($c > c_D$), and a theory for the electrical conductivity in these “extreme” conditions does not exist. However, highly concentrated systems can be treated, from a pure phenomenological point of view, as a heterogeneous colloidal system in the mean field ap-

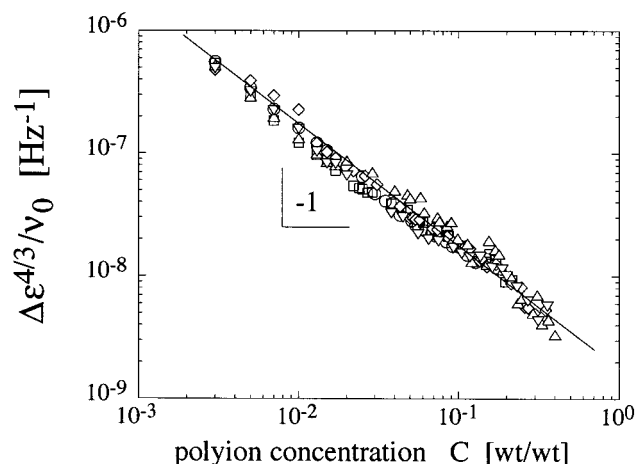


Figure 7. Scaling relationship between the dielectric parameters $\Delta\epsilon$ and ν_0 and the polymer concentration c . For a “good” solvent, a slope of -1 is expected. This dependence is verified for the different molecular weights investigated: (○) 225 kD; (□) 140 kD; (◇) 60 kD; (△) 20 kD; (▽) 5.1 kD.

proximation. By considering the system as being composed of polymer domains randomly dispersed in an aqueous phase to form a “bicontinuous” network, the electrical conductivity can be described within the Looyenga relationship.³² This expression, derived without any assumption about the geometric shape of the disperse polymer domains, can be written as

$$\sigma^{1/3} = \sigma_{\text{aq}}^{1/3}(1 - \Phi) + \sigma_p^{1/3}\Phi \quad (27)$$

where σ_p and σ_{aq} are the conductivity of the polymer and aqueous domains, respectively, and Φ is the fractional volume of the polymer domain in the whole solution. In the presence of counterion condensation, only the fraction f of free counterions contributes, to a first approximation, to the conductivity of the aqueous domain through the expression

$$\sigma_{\text{aq}} = \lambda_c f \frac{C\rho_w}{(1 - C)(MW)_N} \quad (28)$$

where λ_c is the equivalent conductance of free counterions, $(MW)_N$ is the molecular weight of the monomer, and C is the polyion concentration, expressed in wt/wt. From the comparison of eq 25 with the experimental values in the region $c > c_D$, the dependence of f on the polymer concentration can be obtained. Also in this case, f decreases with the polymer concentration. This finding is qualitatively similar, whatever the value for the conductivity of the polymer domain is assumed.

5. Conclusions

We have investigated the salt-free electrical behavior of aqueous solutions of linear, flexible polyelectrolytes (sodium polyacrylate and poly(acrylic acid)), in a wide range of concentrations and molecular weights. Different concentration regimes can be clearly identified, both on the basis of Newtonian viscosity measurement data and on the basis of the electrical conductivity behavior. Two different models for the conductivity of semidilute polyelectrolyte aqueous solutions, based on scaling approaches, were used to estimate the fraction f of free counterions from the conductivity data.

Although these estimates slightly differ in their absolute values, they clearly show that the usual assumption that the effective charge on a polyion chain is independent of the polymer concentration is no longer valid, at least for strongly charged polyelectrolytes. In the very high concentration regime, where presumably electrostatic blobs begin to overlap, a theory to describe the electrical and dielectric behavior of the solution has not been yet completely developed. However, even in this case, an empirical approach based on the effective medium theory approximation shows that a constant level of counterion condensation as the concentration is changed is not in agreement with the experimental findings. From a different point of view, this should not be surprising considering the strong ordering of a bare charge on the surrounding water molecules and the strong change in the quality of water as a solvent that from this order should ensue. It is hoped that the experimental data presented in this study will stimulate theoretical development as well as encourage the use of conductivity measurements as a valuable probe in the evaluation of the effective charge of polyelectrolytes.

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