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Electrical conductivity of aqueous polyelectrolyte solutions in the presence of counterion condensation: The scaling approach revisited

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The conductometric properties of aqueous polyelectrolyte solutions in the absence of added salt are reviewed in the light of the dynamic scaling description of the polymer conformation in different concentration regimes, recently proposed by Dobrynin and Rubinstein [Macromolecules **28**, 1859 (1995); **32**, 915 (1999)]. The scaling approach to the transport properties of polyelectrolyte solutions allows us to separate contributions due to polymer conformation from those due to the ionic character of the chain, and offers the possibility to extend the validity of the Manning conductivity model to the dilute and semidilute regimes. Moreover, the quality of the solvent, influencing the polyion-counterion interactions, can be properly taken into account. The electrical conductivity predicted by this scaling approach compares reasonably well with the observed values for a model polyelectrolyte (polyacrylate sodium salt in aqueous solutions, good solvent condition) over an extended concentration range from the dilute to the semidilute regime.

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I. INTRODUCTION

The transport properties of aqueous polyelectrolyte solutions, both in the presence and in the absence of added salt, differ from those of neutral macro-molecular solutions and those of simple electrolytes, owing to the strong electrostatic interactions between counterions in the bulk solution and charged groups on the polyion chain [1–4]. This peculiar behavior, whose specificity lies in the combination of properties derived from long-chain polymers and those derived from charge interactions, despite having been extensively investigated both theoretically and experimentally, is still not completely understood.

The current models for polyelectrolyte solutions are generally based on counterion condensation, first introduced by Imai and Onishi [5], Oosawa [6], and later by Manning [7,8], for an infinitely long and thin line charged chain. The basic idea is that if the energy density of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy K_BT.

Although the main results based on the Manning counterion condensation model [7–10] are fairly well satisfied by experimental data, they are valid only at infinite dilution. When the polyion concentration is progressively increased, effects associated with the polymer chain conformation become relevant and their influence on the overall electrical properties of the polyelectrolyte solutions must be properly considered.

An interesting property of these systems, not completely understood despite increasing theoretical and experimental effort, is the strong correlation between the shape (or conformation) of the polymer chain in solution and its ionic state and *vice versa*. Moreover, the poor or good solvent conditions, influencing the electrostatic polyion-counterion interactions contribute to making the analytical description of these systems very complicated and far from being satisfactory when theory is compared with experimental results in a wide range of polymer concentrations.

The long-range electrostatic interactions introduce characteristic length and time scales which vary with the polymer concentration, covering the dilute, semidilute, and concentrated regimes. These scaling lengths make the application of the scaling description possible.

Although scaling concepts [11–13] have been applied to polyelectrolyte solutions many years ago, more recently Dobrynin, Colby, and Rubinstein [14] proposed a description of the dynamics of charged polymer chains in a different concentration regime on the basis of two scale lengths, i.e., when the chain is shorter than the electrostatic screening length and when it is larger than the correlation length. These scaling lengths define different concentration regimes to which different chain conformations correspond and, finally, different counterion-polyion interactions. Since scaling theory takes into account the conformational changes of the chain in different concentration regimes, contributions to the transport properties due to interactions of counterions with polymer chains can be properly accounted for within this approach.

Starting from the expression of the polyion equivalent conductance originally derived by Manning [15] in the very high dilution limit and in the presence of counterion condensation, we have extended this approach [16], on the basis of the scaling picture, to more concentrated systems, from the dilute regime, where stretched rodlike configurations prevail, to the semidilute regime, where a random walk statistics applies to the chain conformation.

In the present paper, we present a review of the electrical conductivity behavior of aqueous polyelectrolyte solutions in the light of the scaling approach proposed by Dobrynin, Colby, and Rubinstein [14] and more recently by Dobrynin

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and Rubinstein [17,18], giving appropriate expressions for the polyion equivalent conductance in the dilute and semidilute regimes, taking into account the influence of the solvent quality (poor or good solvent conditions).

These expressions, based on the electrical conductivity treatment of the counterion condensation proposed by Manning [15], represent an extension of this model towards a higher concentration regime, where conformational chain effects begin to contribute.

Moreover, we suggest a means to evaluate the fraction of free counterions and the solvent quality parameter from dielectric spectroscopy measurements in the radio wave frequency range, independently of the electrical conductivity measurements [19]. The knowledge of these quantities allows us to consider appropriate expressions for the electrical conductivity both in the dilute and semidilute regimes, taking into account the hydrophobicity of the polymer chain. A preliminary comparison with the electrical conductivity values obtained for a typical model polyelectrolyte chain in good solvent condition (polyacrylate sodium salt in aqueous solution) over an extended concentration range provides further support to the use of scaling concepts to explain the transport properties of strongly charged, flexible polyelectrolytes in aqueous solutions.

II. THEORETICAL BACKGROUND

Electrical conductivity, originated by the movement of any charged entity in response to an external electric field, can be broken essentially into the product of three different terms, i.e., the charge ze (z is the valence and e the elementary charge), the numerical concentration n of each carrier, and its mobility u, defined as the ratio of the average velocity to an applied electric field of unit strength.

The overall electrical conductivity, induced by a uniform electric field applied to charged particles uniformly dispersed in a continuous (conducting or nonconducting) medium, due to the sum of contributions of all the carriers in the system, is given by

$$\sigma = \sum_i (|z_i|e) n_i u_i . \tag{1}$$

From an experimental point of view, the usual definition of the electrical conductivity σ is given by a linear relationship,

$$\langle \vec{J} \rangle = \sigma \vec{E}, \tag{2}$$

between the volume-averaged current density

$$\langle \vec{J} \rangle = \frac{1}{V} \int_V \vec{J}(\vec{r}) dv \tag{3}$$

and the measured electric field

$$\vec{E} = -\frac{1}{V} \int_V \nabla \psi(\vec{r}) dv, \tag{4}$$

where $\psi(\vec{r})$ is the electrical potential at position $\vec{r}$ and V is a sufficiently large volume of the system. Equation (1) can be rewritten in the usual way (in cgs units) as

$$\sigma = \sum_i z_i C_i \lambda_i , \tag{5}$$

where C_i are the concentrations (in mol/cm^3) and λ_i are the equivalent conductances (in statohm cm^2 mol^{-1}) of each charged carrier present in the system.

We will apply Eq. (5) to the system under investigation. Consider a polyelectrolyte solution made up of polyion chains, each of them with a degree of polymerization N, contour length l, monomer size b at a concentration N_p (in mol/cm^3) dispersed in an aqueous medium (a simple water phase or a simple salt aqueous electrolyte solution) of electrical conductivity σ_0. In principle, in aqueous media, also present are H^+ and OH^- ions, provided by the dissociation of water. Under the conditions considered, their concentrations are of the order of 10^{-7} mol/l and their presence will be neglected.

Owing to interactions between polyions and counterions (derived from the ionization of the charged groups on the polyion chain), the transport (and thermodynamic) properties of the solution are strongly influenced. At finite concentration, some counterions, owing to the interplay between the electrostatic interactions and the change in entropy due to their spatial confinement may condense on the polyion itself. According to the Manning condensation model [7,8,15], the conductivity behavior of the overall system is characterized by a charge-density parameter ξ defined as

$$\xi = \frac{l_B}{b} = \frac{e^2 |z_p|}{\epsilon_w K_B T b}, \tag{6}$$

where ϵ_w is the dielectric constant of the aqueous phase, $K_B T$ is the thermal energy, and $b = l/N$ is the average spacing between charged groups on the polyion chain, and z_p is the valence of the polyion charged groups. In particular, if the charge distance is less than the Bjerrum length $l_B = e^2/\epsilon_w K_B T$ ($l_B = 7$ Å at $T = 25\,°\mathrm{C}$ in water), the electric field becomes so strong that counterions, of valence z_1, become trapped close to the polyion chain (counterion condensation) and a fraction $(1-f) = 1 - 1/\xi(|z_1 z_p|)$ will condense on the polyion chain to reduce its effective charge to a critical value corresponding to $\xi_c = 1/|z_1 z_p|$. Owing to this effect, each polyion bears an electric charge $Q_p = z_p e N f$ and releases in the aqueous phase a number Nf of counterions. Electroneutrality of the solution imposes $Q_p = z_1 e f N$ that defines the sign of z_1 to be opposite to that of z_p. In the absence of added salt and in the presence of counterion condensation, Eq. (5) reads

$$\sigma = z_1 C_1 \lambda_1 + z_p C_p \lambda_p , \tag{7}$$

where the subscripts 1 and p refer to counterions and polyions, respectively. For univalent counterions ($z_1 = 1$), the following relationships hold, i.e., $z_p = Nf$, $C_p \equiv N_p$, $C_1 = N f N_p$ and Eq. (7) becomes

$$\sigma = N f N_p (\lambda_1 + \lambda_p). \tag{8}$$

Equation (8) depends on three parameters, the fraction f of free counterions and the equivalent conductances λ_1 and λ_p of counterions and polyions, respectively, each of them takes into account the electrical properties of the system.

As far as the counterion equivalent conductance λ_1 is concerned, following the Manning derivation [7,8], we have

$$\lambda_1 = \lambda_1^0 \frac{D_1^u}{D_1^0} - \lambda_p \left(1 - \frac{D_1^u}{D_1^0} \right), \tag{9}$$

where D_1^u and D_1^0 are the diffusion coefficients of counterions in the limit of infinite dilution and in the presence of polyions and λ_1^0 is the equivalent conductance of free counterions. With this substitution, Eq. (8) becomes

$$\sigma = N f N_p \frac{D_1^u}{D_1^0} (\lambda_1 + \lambda_p), \tag{10}$$

Manning derived for D_1^u / D_1^0 the value 0.866.

The equivalent conductance $\boldsymbol{\lambda_p}$

The equivalent conductance λ_p can be written as the ratio of the total charge Q_p on the polyion chain and the total electrophoretic coefficient f_{Etot}

$$\lambda_p = F u_p = F \frac{Q_p}{f_{\mathrm{Etot}}}, \tag{11}$$

where $F = e\mathcal{N}$ is the Faraday number, with $\mathcal{N}$ being the Avogadro number. According to Manning [7,8], the total electrophoretic coefficient f_{Etot}, corrected for the "asymmetry field" effect, can be written as

$$f_{\mathrm{Etot}} = \frac{f_E + \dfrac{Q_p}{u_1^0} \left(1 - \dfrac{D_1^u}{D_1^0} \right)}{\dfrac{D_1^u}{D_1^0}}, \tag{12}$$

where u_1^0 is the counterion mobility in the aqueous phase (without polyions) and f_E is the usual electrophoretic coefficient.

If the polyion is modeled as an ensemble of N_b simple (spherical) structural units of radius R_b, taking into account the effect due to hydrodynamic interactions (both between the simple structural units and the pure solvent and between different units in the same chain), the electrophoretic coefficient can be written, according to the general expression given by Kirkwood and Riseman [20], as

$$f_E = \frac{N_b \zeta_b}{1 + \dfrac{\zeta_b}{6\pi\eta N_b} \displaystyle\sum_i^{N_b} \sum_{j \neq i}^{N_b} \langle r_{ij}^{-1} \rangle}, \tag{13}$$

where $\zeta_b = 6\pi\eta R_b$ is the friction coefficient, with η being the viscosity of the aqueous phase and r_{ij} being the distance between different structural units (along the same chain). Within this scheme, the resulting equivalent polyion conductance λ_p is given by

$$\lambda_p = \frac{F Q_p \dfrac{D_1^u}{D_1^0}}{f_E + \dfrac{D_1^u}{D_1^0} \left(1 - \dfrac{D_1^u}{D_1^0} \right)}. \tag{14}$$

By introducing an appropriate cutoff function and the assumption of a full-extended polyion chain ($r_{ij} = |i-j|b$), the electrophoretic friction coefficient [Eq. (13)], calculated following Manning [7,8,15], yields

$$f_E = \frac{N_b \zeta_b}{1 + \dfrac{\zeta_b}{3\pi\eta b} |\ln(k_D b)|} \approx \frac{3\pi\eta N_b b}{|\ln(k_D b)|}, \tag{15}$$

where $k_D = (4\pi b N N_p)^{1/2}$ is the inverse of the Debye screening length. The final expression for the electrical conductivity of a salt-free polyelectrolyte solution in the presence of counterion condensation, within the Manning model [15], reads

$$\sigma = N N_p f \frac{D_1^u}{D_1^0} \left(\lambda_1^0 + \frac{F z e N f \dfrac{D_1^u}{D_1^0}}{\dfrac{z e N f}{u_1^0} \left(1 - \dfrac{D_1^u}{D_1^0} \right) + \dfrac{3\pi\eta N_b b}{|\ln(k_D b)|}} \right). \tag{16}$$

The extension of the above model to more concentrated systems is based on a scaling picture of the chain conformation of a polyelectrolyte solution in the dilute and semidilute regimes in the absence of added salt. We will follow the scaling approach given by Dobrynin, Colby, and Rubinstein [14] and Dobrynin and Rubinstein [18,17].

III. THE SCALING PICTURE

Scaling concepts, successfully used for systems containing uncharged polymers, have been applied to polyelectrolyte solutions by de Gennes [11] and Odijk [13] and, more recently, by Dobrynin, Colby, and Rubinstein [14]. Since the scaling theory takes into account the conformational changes of the polymer chain in different concentration regimes, it provides the necessary means to evaluate the chain slope contribution to the transport behavior of the system. In Fig. 1, we summarize, using the notation of Dobrynin, Colby, and Rubinstein [14] and Dobrynin and Rubinstein [17], the meaning of the different scale lengths and the main chain conformation predicted by the scaling model, both for good solvent and poor solvent conditions.

A. Dilute solutions

At very low concentration, in the dilute regime, the Debye screening length k_D^{-1} is much larger than the distance between chains and charges interact via the unscreened Coulombic potential. The polymer chain is represented by an extended rodlike configuration of N_D electrostatic blobs of size D to form a fully extended chain of length $L = N_D D$. Each electrostatic blob contains g_e monomers and bears an electric charge $q_D = z e f g_e$ (f is again the fraction of ionized

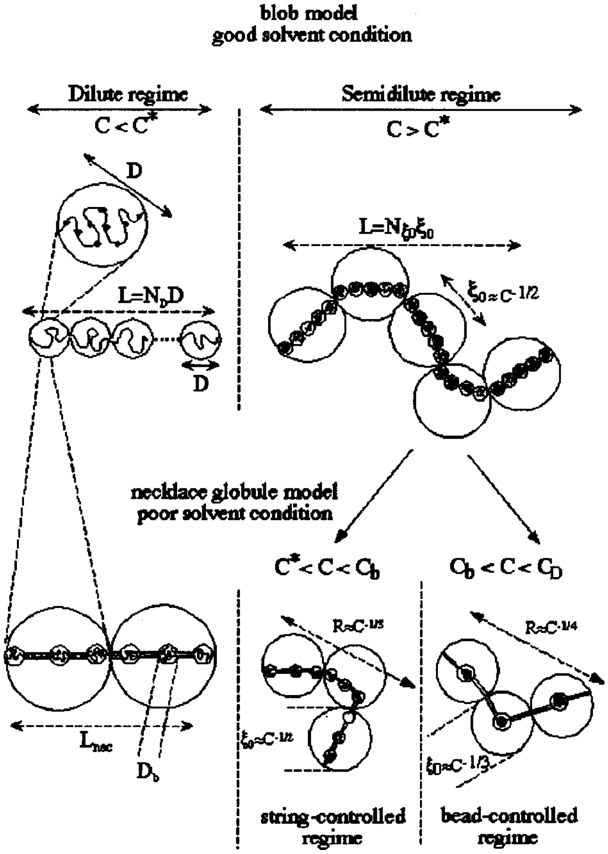

FIG. 1. A sketch of a polyelectrolyte chain in poor and good solvent conditions, for different (salt-free) concentration regimes. The chain is an extended (rodlike) configuration of electrostatic blobs and a random walk of correlation blobs in good solvent condition for dilute and semidilute regimes, respectively, and a chain of globules connected by strings (necklace model) in poor solvent condition (proposed by Dobrynin and Rubinstein [14,17,18]).

charged groups on the polyion chain and consequently the fraction of free counterions). The total charge of each polyion chain is $Q_p = N_D q_D = zefg_e N_D$.

In this case, the elementary unit that contributes to the overall friction coefficient is the electrostatic blob (instead of the “elementary unit” in the Manning model). Using a cutoff function $\exp(-r_{ij}/N_D D)$ in order to neglect contributions for $r_{ij} > N_D D$ and following the Manning derivation given in Ref. [15], Eq. (15) reduces to

$$f_E = \frac{N_D \zeta_D}{1 + \dfrac{\zeta_D}{3\pi\eta D}\ln(N_D)} \approx \frac{3\pi\eta N_D D}{\ln(N_D)}. \tag{17}$$

The full expression for the electrical conductivity in this concentration regime and in a good solvent condition reads

$$\sigma = N N_p f \frac{D_1^u}{D_1^0}\left(\lambda_1^0 + \frac{F z e N f \dfrac{D_1^u}{D_1^0}}{\dfrac{z e N f}{u_1^0}\left(1 - \dfrac{D_1^u}{D_1^0}\right) + \dfrac{3\pi\eta N_D D}{\ln(N_D)}} \right). \tag{18}$$

B. Semidilute solutions

In the semidilute solutions, the polyion chain is modeled as a random walk of N_{ξ_0} correlation blobs of size ξ_0, each of them containing g monomers. Each blob bears an electric charge $q_{\xi_0} = zefg$ and the full chain, of contour length $L = N_{\xi_0}\xi_0$, bears a charge $Q_p = N_{\xi_0} q_{\xi_0} = zefgN_{\xi_0}$. Due to the strong electrostatic interactions, within each correlation blob, the chain is a fully extended conformation of electrostatic blobs. This means that for $r < \xi_0$, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size D), and for $r > \xi_0$, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0.

In this case, the electrostatic friction coefficient for a random walk of N_{ξ_0} blobs is given by

$$f_E = \frac{N_{\xi_0}\zeta_\xi}{1 + \dfrac{\zeta_\xi}{6\pi\eta N_{\xi_0}} \displaystyle\sum_i \sum_{j \neq i} \langle r_{ij}^{-1} \rangle} = \frac{N_{\xi_0}\zeta_\xi}{1 + \dfrac{8}{3}\sqrt{N_{\xi_0}} \dfrac{\zeta_\xi}{\sqrt{6\pi^3}\,\eta\xi_0}}, \tag{19}$$

where the average friction coefficient ζ_ξ (associated with a single rodlike unit of size ξ_0), formed by N_{ξ_0}/N_D spheres of size D, can be derived on the basis of the scaling properties from Eq. (17), with the substitution of $N_D D$ with ξ_0 and N_D with $N_D/N_{\xi_0} = g/g_e$, i.e.,

$$\zeta_\xi = \frac{3\pi\eta\xi_0}{\ln(g/g_e)}. \tag{20}$$

In this case, for good solvent conditions, the full expression for the electrical conductivity reads

$$\sigma = N N_p f \frac{D_1^u}{D_1^0}\left(\lambda_1^0 + \frac{F z e N f \dfrac{D_1^u}{D_1^0}}{\dfrac{z e N f}{u_1^0}\left(1 - \dfrac{D_1^u}{D_1^0}\right) + \dfrac{N_{\xi_0}\zeta_\xi}{1 + \dfrac{8}{3}\sqrt{N_{\xi_0}}\,\zeta_\xi/\sqrt{6\pi^3}\,\eta\xi_0}} \right), \tag{21}$$

with ζ_ξ given by Eq. (20).

This scaling picture has been more recently revisited by Dobrynin and Rubinstein [18,17], who analyzed the configuration of a hydrophobic chain in a poor solvent condition, within the so-called necklace globule model [17]. In this case, due to strong hydrophobic interactions between the hydrocarbon backbone and water molecules, the electrostatic (or correlation) blobs in a poor solvent condition will split into a set of smaller charged globules (beads) connected by long and narrow sections (strings). Moreover, whereas in the dilute regime a unique configuration prevails, the semidilute regime ($c^* < c < c_D$) splits into a string-controlled ($c^* < c < c_b$) and a bead-controlled ($c_b < c < c_D$) regime, where a different concentration dependence of the chain size appears.

We recall here a brief review of the main theoretical predictions of the necklace model concerning the behavior of a polyelectrolyte chain under poor solvent conditions ($T < \theta$), following the derivation given by Dobrynin and Rubinstein [17,18].

When the total effective charge of a chain $Q_1 = zefN$ becomes larger than $ze(N\tau b/l_B)^{1/2}$ and Coulomb repulsion becomes comparable to the surface energy, the system reduces its total free energy giving rise to N_b beads of size D_b containing g_b monomers each and joined $(N_b - 1)$ strings of length l_s. Here, θ is the temperature at which the net excluded volume for uncharged monomers is zero and the solvent quality parameter is defined as $\tau = (\theta - T)/\theta$. The length L_n of the necklace is given by $L_n = N_b l_s$, since most of the length is stored in the strings ($l_s > D_b$).

In the semidilute regime, a new characteristic length appears when the correlation length ξ_0 becomes of the same order of magnitude at the length l_s of the string between neighboring beads. The overlapping concentration c_b is given by

$$c_b \approx b^{-3}\tau^{-1/2}(l_B/b)^{1/2} f. \tag{22}$$

In the range $c^* < c < c_b$, the chain is assumed to be a random walk of $N_{\xi_0} = N/g_\xi$ correlation segments of size ξ_0, each of them containing g_ξ monomers. The size of the random walk chain is

$$R \approx \xi_0 \left(\frac{N}{g_\xi}\right)^{1/2} \approx bN^{1/2}(c_b/c)^{1/4}. \tag{23}$$

On the other hand, in the range $c_b < c < c_D$, owing to the screening of the electrostatic interactions between beads, the model predicts only one bead per correlation globule of size ξ_0, containing $g_\xi \approx \tau(l_B/b)^{-1} f^{-2}$ monomers. The crossover concentration is of the order of $c_D \approx \tau b^{-3}$ and the chain size is

$$R \approx \xi_0 \left(\frac{N}{g_\xi}\right)^{1/2} \approx Nb^{1/2}(c_b/c)^{1/3}. \tag{24}$$

Following the above derivation and the appropriate scaling relationships, the electrophoretic friction coefficient f_E can be written as

$$f_E = \frac{3\pi\eta N_b D_b}{1 + \dfrac{D_b}{l_s}|\ln(N_b)|} \tag{25}$$

in the dilute regime ($c < c^*$) and according to Eq. (19) in the semidilute regime ($c > c^*$), where the friction coefficient ζ_ξ is given by

$$\zeta_\xi = \frac{3\pi\eta N_b D_b}{1 + \dfrac{D_b}{l_s}\left|\ln\left(\dfrac{l_s}{\xi_0}\right)\right|} \tag{26}$$

in the string-controlled semidilute ($c^* < c < c_b$) regime and by

$$\zeta_\xi = 3\pi\eta D_b \tag{27}$$

in the bead-controlled semidilute ($c_b < c < c_D$) regime.

C. Scaling relationships and the influence of the solvent quality parameter

Although the main contribution to the electrical conductivity (transport properties) comes from counterions (i.e., from counterion-polyion interactions), the effect due to the conformational change induced by the increase of the polyion concentration cannot be neglected and can be successfully described within the scaling approach.

In the dilute regime and for a good solvent condition, when the polymer chains are stretched and tend to a rodlike configuration of electrostatic blobs, the parameters entering the polyion mobility λ_p are the length of the full extended chain $N_D D$ and the number N_D of blobs in each chain. From the above theory, it appears that the polymer conformation strongly influences the transport properties of the solution and, in particular, the fraction f of free counterions; the electrostatic blob size D and the correlation length ξ_0 play the role of key parameters. According to Dobrynin, Colby, and Rubinstein [14], these quantities scale as

$$N_D D \approx Nb(l_B/b)^{2/7} f^{4/7}, \tag{28}$$

$$N_D \approx N(l_B/b)^{5/7} f^{10/7}. \tag{29}$$

In the semidilute regime and for a good solvent condition, the characteristic parameters are the contour length $N_{\xi_0}\xi_0$ of the random walk chain of correlation blobs, the number N_{ξ_0} of correlation blobs within each polymer chain, and the ratio g/g_e of the monomers inside a correlation blob to those inside an electrostatic blob. Again, according to Dobrynin, Colby, and Rubinstein [14], these quantities scale as

$$N_{\xi_0}\xi_0 = N_D D \approx Nb(l_B/b)^{2/7} f^{4/7}, \tag{30}$$

$$N_{\xi_0} \approx Nb^{3/2} c^{1/2}(l_B/b)^{3/7} f^{6/7}, \tag{31}$$

$$\frac{g}{g_e} \approx b^{-3/2} c^{-1/2}(l_B/b)^{2/7} f^{4/7}. \tag{32}$$

In the case of a poor solvent condition ($T < \theta$), according to the above stated necklace globule model, the characteristic quantities scale as

$$N_b \approx \frac{N}{g_b} \approx N(l_B/b)\tau^{-1} f^2, \tag{33}$$

$$D_b \approx b(l_B/b)^{-1/3} f^{-2/3}, \tag{34}$$

$$l_s \approx b(l_B/b)^{-1/2} f^{-1} \tau^{1/2} \tag{35}$$

in the dilute regime ($c < c^*$); as

$$\xi_0 \approx b^{-1/2} c^{-1/2} \tau^{1/4} (l_B/b)^{-1/4} f^{-1/2}, \tag{36}$$

$$g_\xi \approx \tau^{3/4} (l_B/b)^{-3/4} f^{-3/2} c^{-1/2} b^{-3/2} \tag{37}$$

in the string-controlled semidilute regime ($c^* < c < c_b$); and as

$$\xi_0 \approx c^{-1/3} \tau^{1/3} (l_B/b)^{-1/3} f^{-2/3}, \tag{38}$$

$$g_\xi \approx \tau (l_B/b)^{-1} f^{-2}, \tag{39}$$

in the bead controlled semidilute regime ($c_b < c < c_D$). In the above expressions and throughout the paper, we drop numerical coefficients (of the order of unity) to keep the discussion at scaling level. Here, in all the scaling relationships, c is the polymer concentration expressed as monomers per unit volume ($c = CN\mathcal{N}$).

In the following, we will analyze the expected polyion conductance λ_p in different concentration regimes (dilute and semidilute), considering the effect of the solvent quality parameter. In particular, we will employ the scaling relationships (28), (29) and (30)–(32) for the good solvent condition, in the dilute and semidilute regimes, respectively (blob model), and the relationships (33), (35) and (36), (39) for the poor solvent condition, in dilute and semidilute regimes, respectively (necklace model). It is noteworthy that, owing to the presence of the parameter τ, the above equations are able, at least in principle, to take into account the influence of both the increasing polyion concentration and the quality of the solvent on the effects induced by counterion condensation on the overall electrical conductivity of the polymer solution.

To proceed further, we must evaluate the changes in the ratio D_1^u/D_1^0 due to the scaling approach.

IV. EVALUATION OF THE TERM (D_1^u/D_1^0) AND COMPARISON WITH THE MANNING RESULT

The term D_1^u/D_1^0 entering Eqs. (18) and (21) requires some further comments. In the presence of counterion condensation and in the absence of added salt, Manning [7,8] derived for the diffusion coefficients of free counterions the following expression, in terms of the Fourier components of the electrostatic potential set up by the fixed polyion,

$$\frac{D_1^u}{D_1^0} = 1 - \frac{1}{3} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} [\xi^{-1}\pi(m_1^2+m_2^2)+1]^{-2}, \tag{40}$$

with $(m_1, m_2) \neq (0,0)$ and $\xi = 1/|z_1 z_p|$, in the presence of counterion condensation. Numerical evaluation of Eq. (40) gives a constant value $D_1^u/{}_1^0 \approx 0.866$.

Within the Manning picture, D_1^u/D_1^0 depends on the polymer charge density and on the concentration of free counterions. In the scaling picture, these quantities become $q_D/D = z g_e f e/D$ and $q_{\xi_0}/\xi_0 = zefg/\xi_0$ for the dilute and semidilute regimes, respectively, whereas the concentration of free counterions is $cf = CNf\mathcal{N}$. With these substitutions, Eq. (40) becomes

$$\frac{D_1^u}{D_1^0} = 1 - \frac{1}{3} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \left(\frac{\pi D}{l_B g_e f}(m_1^2+m_2^2)+1 \right)^{-2} \tag{41}$$

for the dilute regime and

$$\frac{D_1^u}{D_1^0} = 1 - \frac{1}{3} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \left(\frac{\pi \xi_0}{l_B g f}(m_1^2+m_2^2)+1 \right)^{-2} \tag{42}$$

for the semidilute regime, respectively. Taking into account the dependences given in Dobrynin, Colby, and Rubinstein's scaling picture [14], we obtain

$$\frac{\xi_0}{g} = \frac{D}{g_e} \approx b(l_B/b)^{2/7} f^{4/7} \tag{43}$$

in the case of good solvent quality. Within the necklace globule model (poor solvent condition), the characteristic quantities D/g_e and ξ_0/g are replaced by $D_b/g_b \approx b(l_B/b)^{2/3} f^{4/3} \tau^{-1}$ in the dilute regime, by

$$\xi_0/g_\xi \approx (l_B/b)^{1/2} b \tau^{-1/2} f \tag{44}$$

in the string-controlled dilute regime, and by

$$\xi_0/g_\xi \approx (l_B/b)^{2/3} c^{-1/3} f^{4/3} \tau^{-2/3} \tag{45}$$

in the bead-controlled semidilute regime, respectively.

Figure 2 shows a comparison between values of D_1^u/D_1^0 according to the Manning theory and those calculated within the scaling model [Eqs. (41) and (42)]. Whereas in the presence of counterion condensation the Manning theory predicts a constant value $D_1^u/D_1^0 = 0.866$, within the scaling model, D_1^u/D_1^0 increases monotonically and the Manning value is reached asymptotically, in the case of a good solvent, only for $\xi \to \infty$ ($f \to 0$). In poor solvent conditions, on the contrary, D_1^u/D_1^0 decreases with the increasing degree of counterion condensation, with a different rate, depending on the value of the solvent quality parameter τ.

V. DEPENDENCE OF THE CONDUCTIVITY ON THE FRACTION *f* AND THE SOLVENT QUALITY PARAMETER τ

As can be seen, from the above analysis it turns out that the electrical conductivity depends on two parameters, the fraction f of free counterions and the solvent quality parameter τ, whose effect on the polymer equivalent conductance

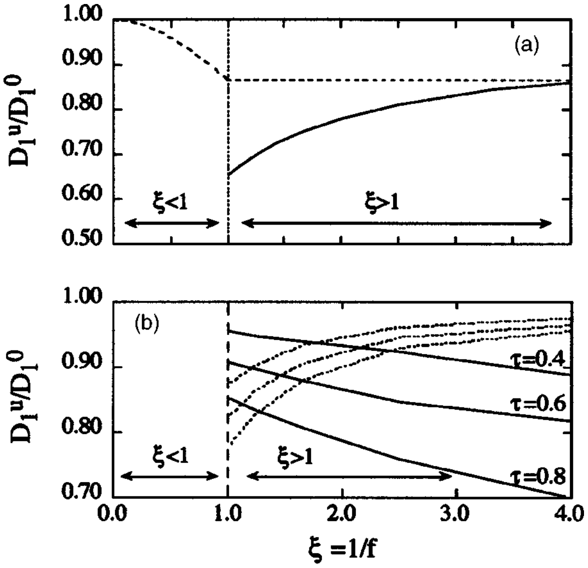

FIG. 2. Counterion self-diffusion coefficient ratio D_1^u/D_1^0 as a function of the charge-density parameter $\xi = 1/f$. Panel (a) values calculated according to the Manning theory. Panel (b) values calculated in the presence of counterion condensation in the case of good solvent (dotted line) and poor solvent (full lines), for three different values of the solvent quality factor, $\tau = 0.4$, $\tau = 0.6$, and $\tau = 0.8$.

λ_p is influenced by the polymer chain conformation (i.e., dilute or semidilute regimes, respectively), according to the above stated scaling model. Figures 3 and 4 show the polyion equivalent conductance λ_p as a function of the fraction f of free counterions in the dilute and semidilute regimes, respectively, compared with the value expected on the basis of the Manning theory. The values are calculated considering the good solvent and poor solvent conditions, separately, according to Eqs. (28), (29) and (30)–(32) for $T > \theta$ in the dilute and semidilute regimes, respectively, and Eqs. (33)–(35) for $T < \theta$ in the dilute regime and Eqs. (36)–(39) for $T < \theta$ in the semidilute (string-controlled and bead-controlled) regime.

The complete behavior of the polyion equivalent conductance λ_p is shown in Figs. 5 and 6, where the dependences on both the fraction f and the parameter τ are considered. Whereas in the dilute regime, in the case of a good solvent, λ_p depends on f only (Fig. 3), in the poor solvent condition, there is a strong influence of the parameter τ (Fig. 5).

In the semidilute regime, there is the further dependence on the polymer concentration C that makes the λ_p behavior more complicated. In the good solvent condition, the situation is depicted in Fig. 6, over an extended concentration

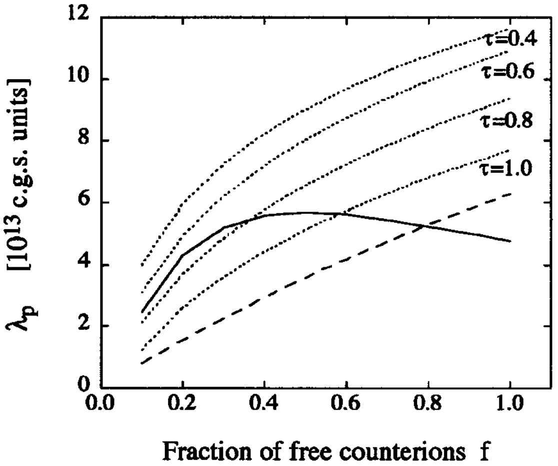

FIG. 3. Polyion equivalent conductance λ_p in the dilute regime as a function of the fraction f of free counterions. Full line, good solvent condition; dotted lines, poor solvent condition for $\tau = 0.4$, $\tau = 0.6$, $\tau = 0.8$, and $\tau = 1.0$; dashed line, λ_p calculated on the basis of the Manning equation, Eq. (14). Values are calculated with $N = 100$, $\eta = 0.01$ P, $u_0^1 = 0.137$ cgs units (Na^+ ion), $b = 3$ Å, $l_B = 7$ Å.

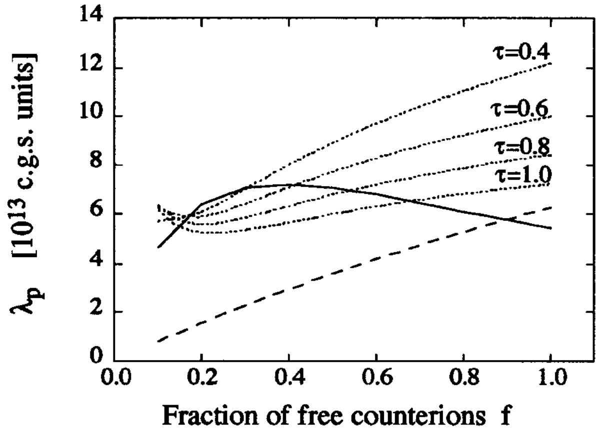

FIG. 4. Polyion equivalent conductance λ_p in the semidilute regime as a function of the fraction f of free counterions. Full line, good solvent condition; dotted lines, poor solvent condition for $\tau = 0.4$, $\tau = 0.6$, $\tau = 0.8$, and $\tau = 1.0$; dashed line, λ_p calculated on the basis of the Manning equation, Eq. (14). Values are calculated with $N = 100$, $\eta = 0.01$ P, $u_0^1 = 0.137$ cgs units (Na^+ ion), $b = 3$ Å, $l_B = 7$ Å. The polyion concentration is 5×10^{20} monomers/cm^3.

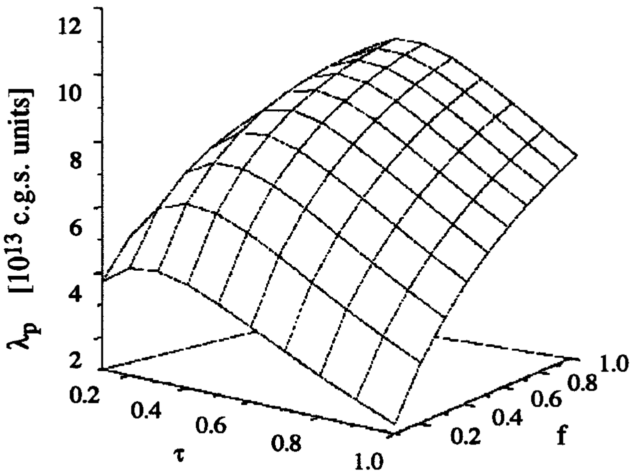

FIG. 5. Polyion equivalent conductance λ_p in the dilute regime as a function of f and τ (poor solvent condition). Values are calculated with $N = 100$, $\eta = 0.01$ P, $u_0^1 = 0.137$ cgs units (Na^+ ion), $b = 3$ Å, $l_B = 7$ Å.

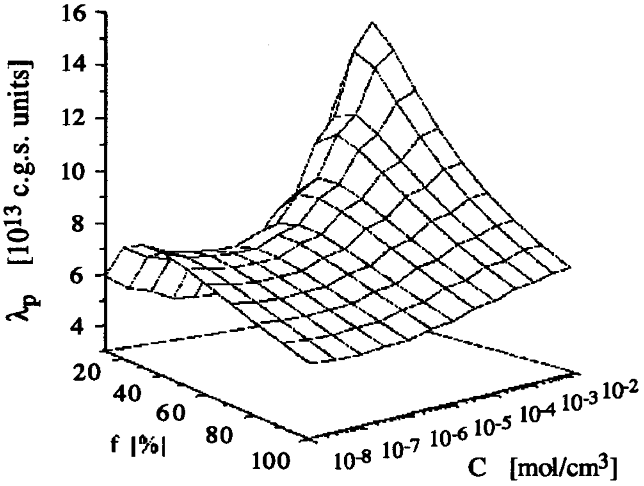

FIG. 6. Polyion equivalent conductance λ_p in the semidilute regime as a function of f and polyion concentration C (good solvent condition). Values are calculated with $N=100$, $\eta=0.01$ P, $u_0^1=0.137$ cgs units (Na$^+$ ion), $b=3$ Å, $l_B=7$ Å.

range, from 10^{-8} to 10^{-2} mol/cm^3. This concentration range certainly exceeds the semidilute range, where Eq. (21) holds, extending towards the limit of the dilute regime on one side and towards the concentrated regime on the other side.

It is noteworthy to analyze the dependence of λ_p in both the dilute and semidilute regimes as a function of the concentration C, for poor and good solvent conditions (Fig. 7). As can be seen, whereas in the dilute regime λ_p is independent of C (either for $T>\theta$ or $T<\theta$), in the semidilute regime it depends markedly on C, showing the presence of a crossover region between the two regimes, where both Eqs. (18) and (21) do not apply. In Fig. 7, for each curve, the high-concentration side (dilute regime) has been connected with the corresponding low-concentration side (semidilute regime) by a continuously smooth line, evidencing the presence of a crossover region. This crossover depends on the degree of polymerization N.

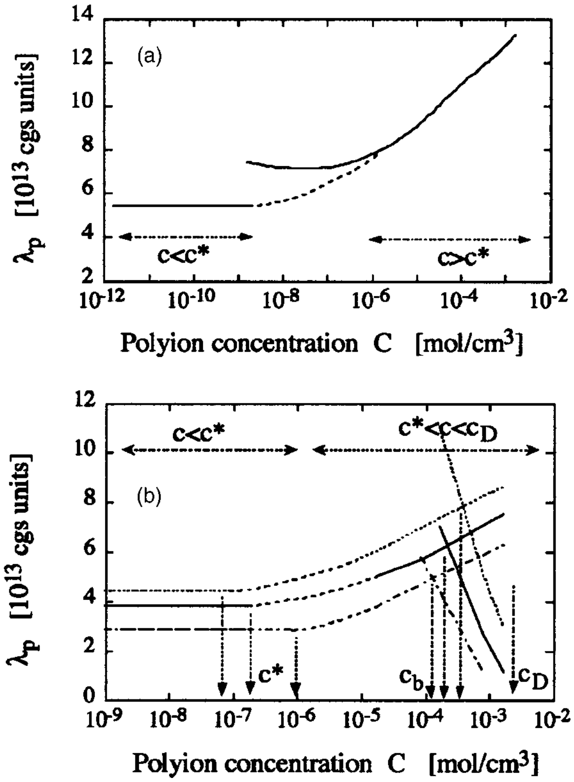

FIG. 7. Polyion equivalent conductance λ_p as a function of the polyion concentration C in the dilute and semidilute regime. Panel (a) good solvent condition (blob model). The fraction of free counterions is fixed to the value $f=0.4$. The dashed line connects the values through a crossover region between the dilute and semidilute regimes. Panel (b) poor solvent condition (necklace model). λ_p has been calculated for three different values of the fraction of free counterions, $f=0.1$ (dotted line), $f=0.2$ (full line), and $f=0.4$ (dotted continuous line). The dashed line indicates a transition region from dilute to semidilute regimes. The arrows mark the characteristic concentrations associated with the different regimes, i.e., c^* between dilute and semidilute regimes, c_b between string-controlled and bead-controlled regimes, and c_D between semidilute and concentrated regimes. These concentrations depend on the fraction f of free counterions, according to the scaling relationships.

VI. COUNTERION CONDENSATION INDUCED BY POLYMER CONCENTRATION OR BY THE QUALITY OF THE SOLVENT

In the above analysis, we have considered the dependence on the polymer concentration C and the fraction f of free counterions, independently, according to the point of view of the counterion condensation model. On the contrary, the fraction f of free counterions could depend on the polymer concentration. As pointed out by Dobrynin and Rubinstein [18], by increasing the polymer concentration or by changing the quality of the solvent, a change of the counterion condensation is provoked. For example, for polyelectrolyte solutions in good or θ solvents, the fraction of free counterions decreases logarithmically with increasing polymer concentration [21].

In what follows, we will discuss the influence of the solvent quality factor and the polymer concentration on the conductometric properties of the polyelectrolyte solution (in the semidilute regime).

This can be done since we have recently proposed [19] that a possible evaluation of the fraction f of free counterions and the solvent quality parameter τ derives from the dielectric relaxation of a polyelectrolyte solution 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 aqueous phase occurs, a well-defined dielectric contribution appears, associated with the mobility of free counterions.

In the semidilute regime, this dielectric dispersion is characterized [22] by a counterion fluctuation on a scale of the correlation length ξ_0, resulting in a dielectric increment $\Delta\epsilon \approx fcl_B\epsilon_w\xi_0^2$ and a relaxation frequency $\nu_0 \approx D_1^0/\xi_0^2$. Taking into account the scaling for the correlation length ξ_0 (in a poor solvent condition) [Eq. (36)], our final result reads

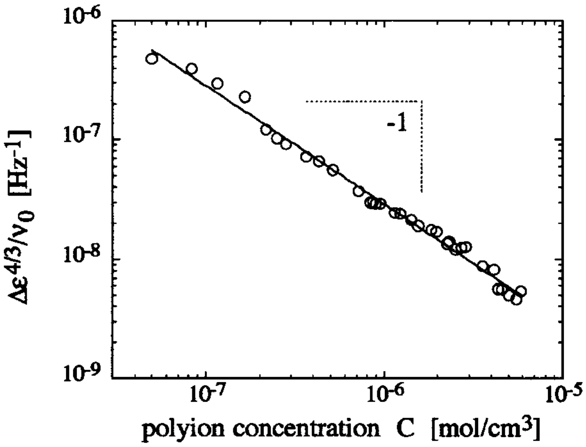

FIG. 8. Scaling relationship between the dielectric parameters $\Delta\epsilon$ and ν_0 of the dielectric relaxation of polyacrylate sodium salt aqueous solution (molecular weight 60 kD) and the polymer concentration C. For good solvent condition, the expected scaling exponent is -1 [Eq. (46)].

$$\tau=\left(\frac{l_B}{b}\right)^{-1/3}\frac{\Delta\epsilon f^{1/3}}{\epsilon_w}, \tag{46}$$

$$f=\frac{\pi\nu_0\Delta\epsilon}{3D_1^0 C l_B\epsilon_w}, \tag{47}$$

where $\Delta\epsilon$ and ν_0 are the measured parameters (the dielectric increment and the relaxation frequency, respectively) of the observed intermediate dispersion and ϵ_w is the permittivity of the aqueous phase.

Both the solvent quality parameter τ and the fraction f of free counterions can be obtained from the dielectric parameters $\Delta\epsilon$ and ν_0, which provide a simple means to estimate these parameters, independently of the conductivity behavior.

VII. COMPARISON WITH EXPERIMENTS

We have recently measured the electrical conductivity [23] and the radiowave dielectric properties [24] of polyacrylate sodium salt aqueous solutions in a wide range of polymer concentrations, covering both the semidilute and concentrated regime. These measurements allow the dielectric parameters (the dielectric strength $\Delta\epsilon$ and the relaxation frequency ν_0) to be determined as a function of concentration C. Details will be reported in a forthcoming paper [24]. In the case of a good solvent condition, substitution of Eqs. (44) and (45) into the scaling relationship $\nu_0\approx D_1^0/\xi_0^2$ yields the scaling behavior

$$\frac{\Delta\epsilon^{4/3}}{\nu_0}\approx C^{-1}, \tag{48}$$

which is strictly verified for the polyion investigated (see Fig. 8). This means that for the polymer investigated, good solvent conditions apply. Incidentally, we want to stress that this scaling furnishes the possibility of evaluating the role of the solvent quality factor from dielectric measurements. Moreover, Eq. (45) furnishes the fraction f of free counterions as a function of the concentration C. Once this parameter is known, we can compare the predicted behavior with experimental findings. From Eqs. (18) and (21), we can determine as a function of C the value of λ_p calculated from the experimental values of the conductivity σ, and the dependence of f on C derived from the dielectric measurements. These values are compared with those calculated on the basis of the above scaling model in the case of a good solvent and in the semidilute regime [Eq. (21) together with Eqs. (30)–(32)].

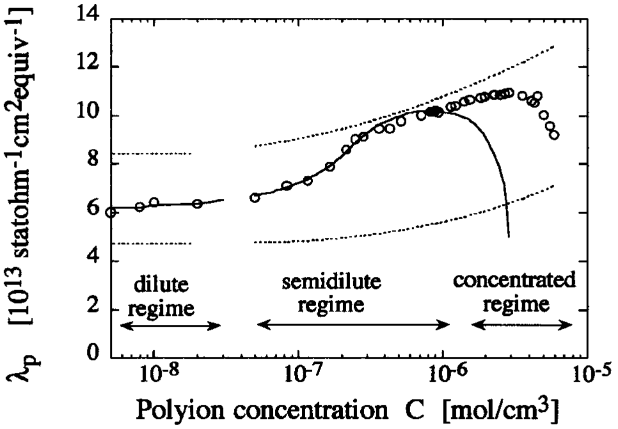

FIG. 9. Comparison between λ_p obtained from the measured electrical conductivity σ of polyacrylate sodium salt solution (in dilute, semidilute, and concentrated regimes) and the values calculated from Eq. (21) with characteristic quantities defined by Eqs. (30)–(32), for good solvent condition. The polymer molecular weight is 60 kD ($N\approx 600$). The fraction f of free counterions (estimated from dielectric measurement) varies from 0.02 to 0.15. The values of λ_p calculated according to Eq. (21) with f constant to the value $f=0.02$ and $f=0.15$ are also shown for comparison.

This comparison is shown in Fig. 9. As can be seen, over the whole semidilute regime, the agreement is quite satisfactory, deviations being markedly evident only at the beginning of the concentrated regime.

VIII. CONCLUSION

We have developed and widely reviewed a simple approach to the electrical conductivity of aqueous polyelectrolyte solutions in the presence of counterion condensation on the basis of the scaling picture recently proposed by Dobrynin, Colby, and Rubinstein [14] and Dobrynin and Rubinstein [18,17]. The polyion equivalent conductance has been calculated along the line proposed by Manning, taking into account hydrodynamic interactions, “charged solvent” effects due to counterelectrophoresis, and the asymmetry field effect, extending its validity to finite polyion concentration, from the dilute to the semidilute regime.

This extension should allow us to apply the Manning theory, valid only for infinite dilution, to more concentrated systems, where the overall electric behavior observed for many polyelectrolyte systems displays a very complex phenomenology, in particular, a dependence of the fraction of free (or condensed) counterions on the polyion concentration. Our approach can be used, moreover, to estimate the fraction f of free counterions from conductivity data, provided that the solvent quality is known, or, conversely, to estimate the conductivity both in the dilute and semidilute regimes if the parameters f and τ can be deduced from radio-wave dielectric relaxation measurements.

APPENDIX

The polyion equivalent concuctance λ_p [Eq. (14)], neglecting the asymmetry field effect, reduces to

$$\lambda_p = F\frac{Q_p}{f_E} \tag{A1}$$

yielding the following expressions.

(i) In the Manning model

$$\lambda_p = \frac{FzNef}{3\pi\eta N_b b}\left|\ln(k_D b)\right|, \tag{A2}$$

where the polyion behaves as a single structural (spherical) unit of size b (distance between two neighboring charges) bearing a single charge ze, and λ_p is corrected by the presence of the logarithmic term.

(ii) In the dilute regime

$$\lambda_p = \frac{FzNef}{3\pi\eta N_D D}\ln(N_D), \tag{A3}$$

where the single structural unit is the electrostatic blob of size D and the correction term is represented by the logarithmic term $\ln(N_D)$. It must be pointed out that the number N_b of charged groups differs from the number of the electrostatic blobs since Eqs. (28) and (33), for good and poor solvents, respectively, hold.

(iii) In the semidilute regime

$$\lambda_p = \frac{FzNef}{3\pi\eta N_{\xi_0}\xi_0}\ln\left(\frac{g}{g_e}\right)\left(1 + \frac{8\pi}{\sqrt{6\pi^3}\dfrac{\sqrt{N_{\xi_0}}}{\ln\left(\dfrac{g}{g_e}\right)}}\right). \tag{A4}$$

On the basis of the same scaling theory discussed above, Colby *et al.* [25] have recently proposed that the conductivity of a polyelectrolyte solution in the absence of added salt could be described by taking into account a polyion equivalent conductance given by

$$\lambda_p = \frac{q_{\xi_0}\ln(\xi_0/D)}{3\pi\eta N_{\xi_0}\xi_0}. \tag{A5}$$

With the equivalence $q_{\xi_0} = zefg$ and under the conditions $g = N/N_{\xi_0}$ and $\xi_0/D = N_D/D = g/g_e$, Eq. (A3) reduces to

$$\lambda_p = \frac{FzNef}{3\pi\eta N_{\xi_0}\xi_0}\ln\left(\frac{g}{g_e}\right), \tag{A6}$$

which equals Eq. (A2) in the limit of large N_{ξ_0}. The expression given by Colby *et al.* [25] is derived within the same scaling scheme described here, neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units (the correlation blobs, in this case) and neglecting the asymmetry field effect. In fact, with the above assumptions, the electrophoretic coefficient is simply

$$f_E = N_{\xi_0}\zeta = N_{\xi_0}\frac{3\pi\eta\xi_0}{\ln\left(\dfrac{g}{g_e}\right)}. \tag{A7}$$

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