PHYSICAL REVIEW E **68**, 011805 (2003)

Electrical conductivity of polyelectrolyte solutions in the presence of added salt: The role of the solvent quality factor in light of a scaling approach

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(Received 12 February 2003; published 29 July 2003)

The effects of added salt on the electrical conductivity behavior of a polyelectrolyte solution are described in light of the scaling approach recently proposed by Dobrynin and Rubinstein [Macromolecules **28**, 1859 (1995); **32**, 915 (1999)], taking into account the influence of the solvent quality factor. The coupling between the conformation of the chain and the local charge distribution, giving rise to different conductometric behaviors, has been investigated under different conditions, in a wide concentration range of added salt. The polyion equivalent conductances λ_p have been evaluated in different concentration regimes for a hydrophilic polyion in good solvent condition and compared with the experimental values obtained from electrical conductivity measurements. The agreement is rather good in the wide range of concentration of the added salt investigated. In the case of poor solvent conditions, we find the appropriate expressions for the electrical conductivity when the polyion chain consists into collapsed beads alternating with stretched segments in the framework of the necklace globule model.

DOI: 10.1103/PhysRevE.68.011805 PACS number(s): 82.35.Rs

I. INTRODUCTION

Polyelectrolytes are macromolecules that, in aqueous solution, dissociate into a macroion and counterions [1–3]. Due to the presence of charged monomers along the polymer chain and the gain in entropy when counterions are released into the aqueous phase, polyelectrolytes are generally soluble in polar solvents and, in particular, in water, making them a system of fundamental interest in the physics of soft-condensed matter [4,5] as well as in biological systems [6] and they are largely employed for technological applications [7].

Although in the last few decades considerable progress has been made in the understanding of the behavior of polyelectrolytes in aqueous solution, the long-range nature of the electrostatic interactions between polyions and counterions and between different charged groups on the same polymer chain introduces new scale lengths that give rise to a very complex phenomenology, whose description is still rather poor. The fine balance between long-range electrostatic interactions and short-range hydrophobic interactions associated with the influence of the polymer chain flexibility leads to different "nonexpected" conformations, giving rise to transitions among different concentration regimes.

One typical and important feature of these ionic solutions is that if the charge density of the polyion chain is high enough, counterion condensation occurs [8–10], i.e., a fraction of counterions remains located in the vicinity of the polymer domain. This effect, due to the balance between a gain in energy in the electrostatic interaction and a loss of entropy in the free energy, makes the behavior of a polyelectrolyte solution different from the one of a uncharged polymer solution and of a simple electrolyte solution.

We have recently investigated the electrical conductivity behavior [11] of salt-free aqueous polyelectrolyte solutions in light of the scaling approach proposed by Dobrynin, Colby, and Rubinstein [12], taking into account the influence of the quality solvent parameter. We have evidenced how the different polyion conformations in the different concentration regimes, from the dilute to the semidilute-entangled regime, reflects on the low-frequency electrical conductivity, this parameter being related to the movement of any charged entity present in the system. Since the electrical conductivity probes the overall ionic character of the solution, the correlation between the shape (or the conformation) and the counterion distribution, that is a source of the peculiar properties of polyelectrolyte solutions, can be properly investigated.

In the present paper, we extend this scaling approach, following the Dobrynin, Colby, and Rubinstein [12] scheme, to polyelectrolyte solutions with added salt and we calculate the electrical conductivity of a polyelectrolyte solution as a function of the solvent quality and polymer concentration, both in the dilute and in the semidilute regime.

The paper is organized as follows. In Sec. II, we review the main predictions of the scaling theories of a polyelectrolyte chain according to the models developed by Dobrynin, Colby, and Rubinstein [12] and later by Dobrynin and Rubinstein [13] for different concentration regimes, taking into account the solvent quality parameter and, in particular, the phenomena occurring in hydrophobic polymers, described within the so-called necklace globule model. In Sec. III, we present some experimental results for the electrical conductivity of a linear flexible polyelectrolye [sodium polyacrylate (NaPAA)] of molecular weight 225 kD in aqueous solutions in the presence of added salt, while in Sec. IV, we compare our experimental results with the predictions of the above stated theoretical background, in light of the scaling theory

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we have reviewed. Section V concludes with a brief discussion.

Experiments that provide a direct evidence for the different chain conformations in the different concentration regimes, in solvents of different quality (good or poor solvent conditions) are rather difficult since different and strongly correlated effects can mask the contribution associated with the polymer conformation. Among different transport parameters, electrical conductivity, resulting from the contributions of all the charged entities present in the solution, should be able to provide the least ambiguous proof of the influence of the polymer chain conformation on the electrical environment, giving evidence of the correctness of the model.

II. THEORETICAL BACKGROUND

We consider the behavior of a polyelectrolyte solution in the presence of simple salt [z_1^s-z_2^s electrolyte solution at a numerical concentration n_s (molecules per unit volume)], containing polyions at a numerical concentration n_p, with a degree of polymerization N and “structural” monomer size b and a contour length $l=Nb$. Each polyion bears an electric charge fNz_pe and releases in the aqueous phase a number of counterions ν_1Nf, each of them bearing an electric charge z_1e. Moreover, added to the aqueous solution, there are two species of small ions derived from the dissociation of the added salt, whose numerical concentrations are $n_1^s=\nu_1^s n_s$ and $n_2^s=\nu_2^s n_s$. Here, f is the fraction of ionized charged groups on the polymer chain and, consequently, the fraction of free counterions, z_p and z_1 are the valences of charged groups on the polyion chain and counterions, respectively. Finally, z_1^s, z_2^s and ν_1^s, ν_2^s are the valences and dissociation constants of the cations and anions derived from the full dissociation of the added salt. The electroneutrality of the whole solution implies $z_p=\nu_1 z_1$ and $\Sigma_{i=1,2}(z_i^s\nu_i^s)n_s=0$. We assume that the added salt does not take part directly in the ionization of the polyion charged groups and therefore the only effect is to screen the electrostatic interactions.

In such a system, electrical conductivity measurements are expected to provide a useful tool for investigating directly the influence of the polymer conformation on the ion distribution in the whole solution and for the evaluation of the effectiveness of the scaling approach in the description of a polyelectrolyte solution.

A. Electrical conductivity of a polyelectrolyte solution

The electrical conductivity originated by an ensemble of charged particles moving under the influence of an external electric field is due to the contribution of three independent terms, i.e., the electric charge ze that each particle bears, the numerical concentration n, and the mobility u of each carrier, defined as the average velocity normalized to the electric field of unit strength, i.e.,

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

Owing to the partial ionization of the charged groups on the polymer chain (counterion condensation effect), in the presence of added salt, the electrical conductivity of the whole solution can be written, in the usual notations, as

$$\sigma=z_{\mathrm{pol}}C_p\lambda_p+z_1C_1\lambda_1+(z_1^sC_1^s\lambda_1^s+z_2^sC_2^s\lambda_2^s), \tag{2}$$

where λ_p, λ_1, and λ_2 are the equivalent conductance (expressed in statohm cm^2 mol^{-1}) of the polyion and cations and anions deriving from the dissociation of the added salt, respectively, C_p, C_1^s, and C_2^s are their concentrations (expressed in moles per unit volume) and $z_{\mathrm{pol}}=Nfz_p$, z_1, z_1^s, z_2^s their valences, respectively.

According to the Manning condensation theory [9,10], the conductivity behavior of the system is characterized by the charge density parameter ξ defined as the ratio of the Bjerrum length l_B to the average spacing $b=l/N$ between charged groups on the polymer chain

$$\xi=\frac{l_B}{b}=\frac{e^2|z_p|}{\epsilon_wK_BTb}. \tag{3}$$

Here, K_BT is the thermal energy and ϵ_w is the permittivity of the aqueous phase. In particular, if the charge distance along the polymer chain is less than the Bjerrum length (~7 Å at $T=25\,^\circ\mathrm{C}$ in water), the electrostatic interactions are so strong that counterions derived from the ionization of the charged groups on the polymer chain become trapped in the vicinity of the polyion itself and a fraction $(1-f)=1-1/\xi|z_pz_1|$ will condense on the polyion chain to reduce its effective charge to a critical value corresponding to $\xi_c=1/|z_pz_1|$. Consequently, each polyion bears an electric charge $Q_p=z_peNf$ and releases in the aqueous phase $Nf\nu_1$ counterions, each of them of charge z_1e.

The equivalent conductances of the ionic species present in the solution are given by Manning [14], according to the following expressions;

$$\lambda_1=\lambda_1^0\frac{D_1}{D_1^0}-\lambda_p\left(1-\frac{D_1}{D_1^0}\right), \tag{4}$$

$$\lambda_2=\lambda_2^0\frac{D_2}{D_2^0}-\lambda_p\left(1-\frac{D_2}{D_2^0}\right), \tag{5}$$

where λ_i^0 ($i=1$, 2) are the limiting equivalent conductances of species i in the pure solvent and D_i/D_i^0 ($i=1$, 2) are the ratio of the self-diffusion coefficient D_i of species i in the polyion solution to its value D_i^0 in the pure solvent.

Substitution of the above relations (4) and (5) into Eq. (2) results in the following expressions:

$$\begin{aligned}\sigma=&(z_1^s\nu_1^s\lambda_1^0+z_2^s\nu_2^s\lambda_2^0)C_s+NC_p\Bigg\{z_1\nu_1(\lambda_1^0+\lambda_p)\\&-\frac{z_p\xi}{3(\nu_1^s+\nu_2^s)|z_1^sz_2^s|}[z_1^2z_1^s\nu_1^s\lambda_1^0+z_2^2z_2^s\nu_2^s\lambda_2^0\\&+(z_1^2z_1^s\nu_1^s-z_2^2z_2^s\nu_2^s)\lambda_p]\Bigg\}\end{aligned} \tag{6}$$

in the absence of counterion condensation ($\xi<1/|z_pz_1|$) and

$$\sigma=(z_1^s\nu_1^s\lambda_1^0+z_2^s\nu_2^s\lambda_2^0)C_s+NfC_p\Bigg\{z_1\nu_1(\lambda_1^0+\lambda_p)-\frac{z_p}{3(\nu_1^s+\nu_2^s)|z_1^sz_2^s||z_pz_1|}[z_1^2z_1^s\nu_1^s(\lambda_p+\lambda_1^0)+z_2^2z_2^s\nu_2^s(\lambda_2^0-\lambda_p)]\Bigg\} \tag{7}$$

in the presence of counterion condensation ($\xi>1/|z_pz_1|$), respectively.

Equations (6) and (7) are the general expressions for the electrical conductivity of an aqueous polyelectrolyte solution in the presence of added salt. The characteristic parameters entering into Eqs. (6) and (7) are the polyion equivalent conductance λ_p and the fraction f of free counterions, both of them depending on the "microscopic" structure of the ionic solution and, in particular, on the polymer conformation which, in turn, depends on the polyion concentration (different concentration regimes) and on the "effective" charge on the polymer chain, after condensation occurred. This complex interplay between structural and electrical parameters can be also proved by the dependence of the fraction f of free counterions on the polymer concentration c, recently reported by the authors of Ref. [15] for a sodium polyacrylate salt solution investigated from dilute to concentrated regime.

In the following section, we will derive the polyion equivalent conductance λ_p as a function of the polymer concentration c and the solvent quality τ.

B. The polyion equivalent conductance

Taking into account the derivation given by Manning [16], the general expression for the polyion equivalent conductance, corrected for the "asymmetry field" effect, in the presence of added salt, can be written as

$$\lambda_p=\frac{FQ_p\left[\frac{D_1}{D_1^s}-\frac{\nu_1^sz_1^s}{z_1X}\left(\frac{D_2}{D_2^s}-\frac{D_1}{D_1^s}\right)\right]}{f_E+\frac{Q_p}{u_1^s}\left(1-\frac{D_1}{D_1^s}\right)+Q_p\frac{\nu_1^sz_1^s}{z_1X}\left[\frac{1}{u_1^s}\left(1-\frac{D_1}{D_1^s}\right)+\frac{1}{u_2^s}\left(1-\frac{D_2}{D_2^s}\right)\right]}, \tag{8}$$

where f_E is the electrophoretic coefficient (without the asymmetry field correction), $X=Nn_p/n_s\equiv c/n_s$ defines the salt concentration with respect to the polyion concentration ($c=Nn_p$ is the numerical concentration of monomers per unit volume), and u_1^s and u_2^s are the cation and anion mobility in the aqueous phase (in the absence of the polyion). The polyion charge Q_p depends on the charge density parameter, assuming the value $Q_p=z_peNf=z_peN/\xi|z_pz_1|$ in the presence of counterion condensation and the structural value $Q_p=z_peN$ in the absence of counterion condensation.

The electrophoretic coefficient f_E has been derived by Kirkwood [17,18] for an ensemble of N_0 rodlike structural units of size R_0 according to the expression

$$f_E=\frac{N_0\zeta_{R_0}}{1+\frac{\zeta_{R_0}}{6\pi\eta N_0}\sum_i\sum_{i\neq j}\langle r_{ij}^{-1}\rangle}, \tag{9}$$

where $\zeta_{R_0}=3\pi\eta R_0$ is the friction coefficient, with η the viscosity of the aqueous phase and r_{ij} the distance between different structural units. In the Manning picture [16], the structural units are the charged groups (after condensation) on the polyion chain while hydrodynamic interactions are mediated by electrostatic interactions with the surrounding counterion atmosphere that, under the influence of the external electric field, drags the solvent in the opposite direction (charge solvent effect). Within this model, by introducing an appropriate cutoff function $\exp(-K_Dr_{ij})$ and a full extended polyion chain ($r_{ij}=|i-j|R_0$), Eq. (9) gives

$$f_E=\frac{N_0\zeta_{R_0}}{1+\frac{\zeta_{R_0}}{3\pi\eta R_0}|\ln(K_DR_0)|}\cong\frac{3\pi\eta N_0R_0}{|\ln(K_DR_0)|}, \tag{10}$$

where $K_D=(4\pi l_Bfc[z_1^2+(\nu_1^sz_1^{s2}+\nu_2^sz_2^{s2})n_s/(fc)])^{1/2}$ is the inverse of the Debye screening length.

C. The scaling approach

The use of scaling concepts to describe the behavior of a polyelectrolyte solution in the different concentration regimes has been successfully employed for a long time and more recently Dobrynin, Colby, and Rubinstein [12] have extended this approach to polyelectrolytes in good and poor solvent conditions, where the polyion assumes different conformations.

We start with a brief review of the main theoretical predictions for the conformation of a polyelectrolyte chain. Within this scaling approach, the chain conformation is essentially due to a fine balance between electrostatic and hydrophobic interactions, related to the Flory parameter $\tau=(\theta-T)/\theta$, where T is the solvent temperature and θ is the temperature at which the net excluded volume for uncharged monomers is zero. When electrostatic repulsive interactions between charged monomers prevail, polyions adopt an extended conformation such as rigid rods, in which it is convenient for the monomers to assemble into ''blobs,'' and good solvent conditions are achieved ($T \geqslant \theta$). When excluded volume and monomer-monomer interactions give rise to a global attraction between monomers, polyion chain collapses into dense spherical globules, compact coils are expected to occur and poor solvent conditions are achieved ($T < \theta$). In very poor solvent conditions, competition between hydrophobicity and conformational entropy of the polymer backbone causes chain to adopt a pearl necklace conformation.

We will summarize here, using the notations of Dobrynin and Rubinstein [12,13], the main features of their scaling approach. Following these authors, the behavior of polyion chain is characterized by three concentration regimes, each of them associated with a characteristic scale length that identifies a characteristic polyion concentration, i.e., a concentration c^*, at which the distance between chains equals their extended length, and a concentration c_D where the electrostatic blobs begin to overlap and the electrostatic length equals the electrostatic blob size. At the concentration c_e (between c^* and c_D), the polymer chains begin to entangle and the hydrodynamic interactions are screened on length scales larger than the correlation length. In these conditions, Zimm-like dynamics up to the correlation length ξ_0 and Rouse-like dynamics for correlation blobs apply. Consequently, the polymer solution behaves as a dilute solution for $c < c^*$, as a semidilute solution for $c^* < c < c_D$ (in particular, as unentangled semidilute for $c^* < c < c_e$ and as entangled semidilute for $c_e < c < c_D$), and finally as a concentrated solution for $c > c_D$.

In the dilute concentration regime, when the chain becomes flexible, the polyion is represented as a self-avoiding walk of N_{r_B} electrostatic blobs of size r_B inside which the conformation is extended. Each electrostatic blob contains g_B monomers and bears an electric charge $q_{r_B} = z_p e f g_B$. The polyion of contour length $L = (N/g_B) r_B$ assumes a flexible conformation with the end-to-end distance given by

$$R = r_B \left(\frac{N}{g_B} \right)^{3/5}, \tag{11}$$

and bears a charge $Q_p = N_{r_B} q_{r_B}$.

In the semidilute regime, the polyion chain is modeled as a random walk of $N_{\xi_0} = N/g$ correlation blobs of size ξ_0, each of them containing g monomers. The polyion contour length is $L = N_{\xi_0} \xi_0$ and the end-to-end distance is given by

$$R = \xi_0 \left(\frac{N}{g} \right)^{1/2}. \tag{12}$$

The correlation blob bears an electric charge $q_{\xi_0} = z_p e f g$ and the polyion charge $Q_p = q_{\xi_0} N_{\xi_0}$.

In the absence of added salt, for distances less than the correlation length ξ_0, the electrostatic interactions dominate and the chain is a fully extended conformation of electrostatic blobs of size D and, for distances larger than ξ_0, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0. The presence of added salt reduces the electrostatic interactions and in both the two regimes a random walk structure prevails.

For hydrophobic polymers, in poor solvent conditions, by analogy with the shape instability of charged droplets [19], Dobrynin and Rubinstein [13,20] have recently analyzed the polymer configuration within the so-called necklace globule model on the basis of a balance between short-range attraction and long-range repulsion between monomers connected to a chain. In this case, owing to the strong hydrophobic interactions between hydrocarbon chains and water molecules, polyions may be ''unstable'' and the electrostatic (and/or correlation) blobs in a poor solvent condition split into a set of smaller charged globules (beads) connected by long and narrow sections (strings). This model is referred to as ''pearl necklace globule'' model. This approach is supported by computer simulation studies [21–24] addressed to analyze systematically the conformations of a weekly charged polyelectrolyte chain with short-range attraction between monomers. These new polymer conformations introduce in the semidilute regime ($c^* < c < c_D$) a new characteristic concentration c_b that defines two regimes, a string-controlled regime ($c^* < c < c_b$) and a bead-controlled regime ($c_b < c < c_D$), where a different concentration dependence of the chain size appears. Following the derivation given by Dobrynin and Rubinstein [13,20], when the polyion effective charge becomes larger than a critical value and the Coulombic repulsion becomes comparable with the surface energy, the polyion conformation gives rise to N_b beads of size D_b containing g_b monomers each and joined by $(N_b - 1)$ strings of length l_s. The overall length of the polyion is $L_{\mathrm{nec}} = N_b l_s$, since most of the length is stored in the strings ($l_s > D_b$).

In the string-controlled regime ($c^* < c < c_b$), the chain is assumed to be a random walk of size

$$R = \xi_0 \left(\frac{N}{g_{\xi_0}} \right)^{1/2} \approx b N^{1/2} (c_b/c)^{1/4}, \tag{13}$$

composed of $N_{\xi_0} = N/g_{\xi_0}$ correlation segment of size ξ_0, each of them containing g_{ξ_0} monomers. In the bead-controlled regime ($c_b < c < c_D$), the screening of the electrostatic interactions causes one bead per correlation globule with a random walk chain conformation of size

$$R = \xi_0 \left(\frac{N}{g_{\xi_0}} \right)^{1/2} \approx b N^{1/2} (c_b/c)^{1/3}. \tag{14}$$

D. The electrophoretic friction coefficient f_E

Proceeding on such a model, the electrophoretic friction factor f_E, depending on the particular conformation assumed by the polyion chain in its proper concentration regime, must be appropriately evaluated, in light of the above stated scaling models.

The expressions for f_E differ in the different concentration regimes, according to the elementary unit that contributes to the conductivity. Following the procedure adopted by

Manning [16], in the dilute regime, taking into account that the elementary unit is the electrostatic blob of size D and that the cutoff function is $\exp(-r_{ij}/N_D D)$, f_E is given by

$$f_E=\frac{N_D\zeta_D}{1+\dfrac{\zeta_D}{3\pi\eta D}\left|\ln(1/N_D)\right|}\approx\frac{3\pi\eta N_D D}{\ln(N_D)}, \tag{15}$$

where the friction coefficient ζ_D is simply given by

$$\zeta_D=3\pi\eta D. \tag{16}$$

In the semidilute regime, where the single elementary unit is the correlation blob of size ξ_0, the electrophoretic friction coefficient for a random walk of N_{ξ_0} blobs is given by

$$f_E=\frac{N_{\xi_0}\zeta_{\xi_0}}{1+\dfrac{8}{3}\sqrt{N_{\xi_0}}\,\dfrac{\zeta_{\xi_0}}{\sqrt{6\pi^3}\,\eta\xi_0}}, \tag{17}$$

where the friction coefficient ζ_{ξ_0} of the single rodlike structure of size ξ_0 can be derived from Eq. (15) with the substitution of $N_D D$ with ξ_0 and N_D with $N_D/N_{\xi_0}=g/g_e$,

$$\zeta_{\xi_0}=\frac{3\pi\eta\xi_0}{\ln(g/g_e)}. \tag{18}$$

In the poor solvent conditions ($T<\theta$), where the necklace model is applied, the elementary unit is the bead of size D_b, the cutoff function is $\exp(-r_{ij}/L_{\mathrm{elec}})$ and the electrophoretic friction coefficient is given by

$$f_E=\frac{3\pi\eta N_b D_b}{1+\dfrac{D_b}{l_s}\left|\ln(N_b)\right|} \tag{19}$$

in the dilute regime ($c<c^*$), and according to Eq. (17) (random walk of N_{ξ_0} blobs of size ξ_0) in the semidilute regime ($c>c^*$).

In this latter case, the friction coefficient ζ_{ξ_0} depends on the structure of the basic unit of the chain that is an extended structure of size ξ_0 of ξ_0/l_s beads in the semidilute string-controlled regime ($c^*<c<c_b$) and is a correlation blob containing a single bead of size D_b in the semidilute bead-controlled regime ($c_b<c<c_D$). Consequently, the friction coefficient is given by

$$\zeta_{\xi_0}=\frac{3\pi\eta N_b D_b}{1+\dfrac{D_b}{l_s}\left|\ln(l_s/\xi_0)\right|} \tag{20}$$

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

$$\zeta_{\xi_0}=3\pi\eta D_b \tag{21}$$

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

E. The scaling relationships in the presence of added salt and the influence of the solvent quality parameter

Equations (6) and (7) give the electrical conductivity of the whole polyelectrolyte solution once the polyion equivalent conductance λ_p is known. This quantity is influenced by the solvent quality through the different dependences of the characteristic parameters of the scaling model. In the dilute concentration regime, $c_f<c<c^*$, the polymer chain is a self-avoiding walk of electrostatic blobs, inside which the conformation is extended. In the case of good solvent conditions ($T>\theta$), the scaling relationships are

$$r_B\approx f^{-2/7}(l_B/b)^{-1/7}c^{-1/2}b^{-1/2}X_s^{-1/2} \tag{22}$$

$$N_{r_B}\approx Nf^{6/7}(l_B/b)^{3/7}b^{3/2}c^{1/2}X_s^{3/2}, \tag{23}$$

$$\frac{g_B}{g_e}\approx f^{4/7}(l_B/b)^{2/7}c^{-1/2}b^{-3/2}X_s^{-3/2}, \tag{24}$$

with $X_s=[z_1^2+(\nu_1^s z_1^{s^2}+\nu_1^s z_1^{s^2})]n_s/fc$. For uni-univalent salt and univalent counterions, $X_s=(1+2/fX)$, with $X=c/n_s$.

In the semidilute concentration regime, $c^*<c<c_D$, the polyion chain is a random walk of $N_{\xi_0}=N/g$ correlation blobs (that are space filling) and the scaling relationships are

$$\xi_0\approx f^{-2/7}(l_B/b)^{-1/7}c^{-1/2}b^{-1/2}X_s^{1/4}, \tag{25}$$

$$N_{\xi_0}\approx Nf^{6/7}(l_B/b)^{3/7}c^{1/2}b^{3/2}X_s^{-3/4}, \tag{26}$$

$$\frac{g}{g_e}\approx f^{4/7}(l_B/b)^{2/7}c^{-1/2}b^{-3/2}X_s^{3/4}. \tag{27}$$

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

$$N_b\approx N\tau^{-1}(l_B/b)f^2X_s^{-1}, \tag{28}$$

$$D_b\approx b(l_B/b)^{-1/3}f^{-2/3}, \tag{29}$$

$$l_s\approx b(l_B/b)^{-1/2}\tau^{1/2}f^{-1}X_s^{1/2} \tag{30}$$

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

$$\xi_0\approx b^{-1/2}\tau^{1/4}(l_B/b)^{-1/4}f^{-1/2}c^{-1/2}X_s^{1/4}, \tag{31}$$

$$g_{\xi_0}\approx b^{-3/2}(l_B/b)^{-3/4}\tau^{3/4}f^{-3/2}c^{-1/2}X_s^{3/4} \tag{32}$$

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

$$\xi_0\approx(l_B/b)^{-1/3}\tau^{1/3}f^{-2/3}c^{-1/3}X_s^{5/12}, \tag{33}$$

$$g_{\xi_0}\approx(l_B/b)^{-1}\tau f^{-2}X_s^{5/4} \tag{34}$$

in the semidilute regime (bead controlled, $c_b<c<c_D$). In the above expressions, we have dropped numerical coefficients (of the order of unity) to keep the discussion at scaling level. Here, in all the above scaling relationships, c is the polyion

TABLE I. Scaling predictions for the characteristic polyion conformational parameters in the presence of added salt, in the different concentration regimes. R—polyion end-to-end distance; r_B—electrostatic blob size; ξ_0—correlation blob size; N_{r_B}—number of electrostatic blobs in each polyion chain; N_{ξ_0}—number of correlation blobs in each polyion chain. For a uni-univalent salt, $X_s = (1 + 2/fX) = 1 + 2n_s/fc$.

		R	r_B	ξ_0	N_{r_B}	N_{ξ_0}
Good solvent	$c < c_s^*$	$c^{-1/5}X_s^{2/5}$	$c^{-1/2}X_s^{-1/2}$		$c^{1/2}X_s^{3/2}$	
	$c > c_s^*$	$c^{-1/4}X_s^{-1/8}$		$c^{-1/2}X_s^{1/4}$		$c^{1/2}X_s^{-3/4}$
Poor solvent	$c < c_s^*$	$X_s^{-1/2}$	$X_s^{1/2}$		X_s^{-1}	
	$c_s^* < c < c_{b_s}$	$c^{-1/4}X_s^{-1/8}$		$c^{-1/2}X_s^{1/4}$		$c^{1/2}X_s^{-3/4}$
	$c_s^* < c < c_D$	$c^{-1/3}X_s^{-5/24}$		$c^{-1/3}X_s^{5/12}$		$X_s^{-5/4}$

concentration expressed as monomers per unit volume ($c = Nn_p$). As pointed out by Dobrynin and Rubinstein [13], any property A of a hydrophobic solution in the presence of added salt can be deduced from the analogous property A_0 in the absence of added salt using the scaling relation $A = A_0 X_s^{\alpha}$. For example, as pointed out by Dobrynin and Rubinstein [13] for the number of monomers in a bead, the exponent α is $\alpha = 1$ in the string-controlled regime and $\alpha = 5/4$ in the bead-controlled regime. The scaling predictions for the characteristic conformational parameters of the polyion chain in the different concentration regimes, both in good and poor solvent conditions, are summarized in Table I.

On the basis of these scaling relationships, the equivalent conductance λ_p can be appropriately evaluated in each concentration regime, taking into account the solvent quality parameter. Figures 1 and 2 show, in a particular case, the typical behavior of the polyion equivalent conductance λ_p in the dilute regime for good solvent ($T > \theta$) and poor solvent ($T < \theta$) condition.

F. The concentrations of the different regimes in the presence of added salt

In order to compare the scaling predictions with the electrical conductivity values experimentally observed in a given electrolyte solution, we need to know the concentration regime present in the solution. In what follows, we will identify the polyion concentration of the different regimes. These characteristic concentrations, delimiting the different concentration regimes in a polyion solution in the presence of added salt, are governed by a balance between the electrostatic interactions between different polyions and those between different charged groups of the same chain.

In the dilute regime, the concentration c_f where the chains become flexible, occurs when the electrostatic screening length r_{scr} equals the size L of the chain in the extended conformation, i.e.,

$$c_f\left(1 + \frac{2n_s}{fc_f}\right) = N^{-2}b^{-3}B^3. \tag{35}$$

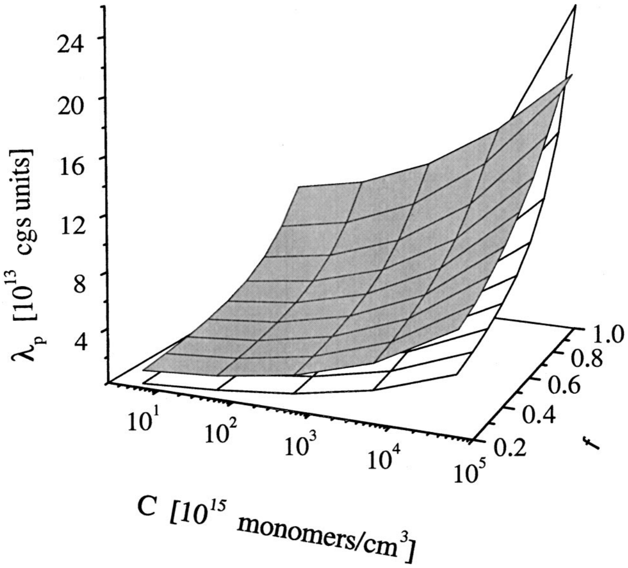

FIG. 1. Polyion equivalent conductance λ_p in the dilute regime as a function of f and polyion concentration c, in the good solvent condition ($T > \theta$). The salt concentration is $X = 0.1$ and $X = 1$ (white and gray symbols, respectively). The values are calculated with the following parameters: $l_B = 7$ Å, $b = 3$ Å, $N = 1000$, $\eta = 0.01$ P, $u_1^s = 0.137$ cgs units, $u_2^s = 0.235$ cgs units.

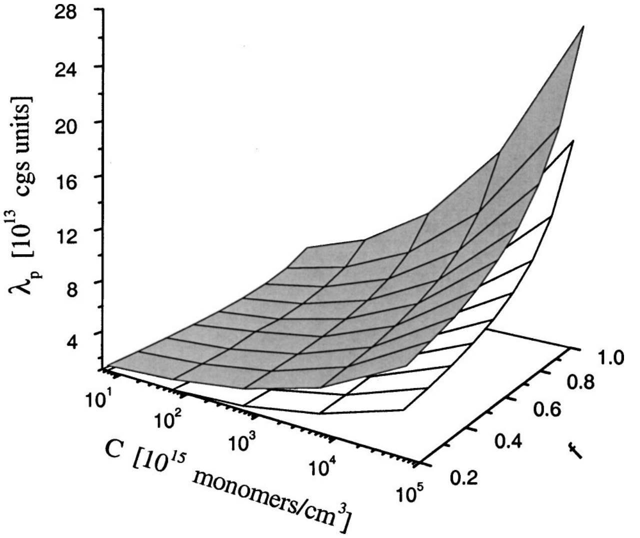

FIG. 2. Polyion equivalent conductance λ_p in the dilute regime as a function of f and polyion concentration c, in the poor solvent condition ($T < \theta$). The salt concentration is $X = 0.1$ and $X = 1$ (white and gray symbols, respectively). The values are calculated with the following parameters: $l_B = 7$ Å, $b = 3$ Å, $N = 1000$, $\eta = 0.01$ P, $u_1^s = 0.137$ cgs units, $u_2^s = 0.235$ cgs units, $\tau = 0.4$.

As the polymer concentration is increased, the concentration c^* is reached when the monomer density within the coil equals the overall monomer density in the solution

$$c^*\left(1+\frac{2n_s}{fc^*}\right)^{-3/2}=N^{-2}b^{-3}B^3. \tag{36}$$

Equation (36) reduces to the usual value in the absence of added salt ($c^*=N^{-2}b^{-3}B^3, n_s=0$) or to the value $c^*=N^{-4/5}(B/b)^{6/5}(2n_s/f)^{3/5}$, in the limit $n_s \gg c$.

At higher polymer concentrations, when the electrostatic screening length equals the electrostatic blob size, the characteristic concentration c_D defines the crossover between the semidilute and concentrated regime

$$c_D\left(1+\frac{2n_s}{fc_D}\right)=b^{-3}B^{-2}. \tag{37}$$

In the poor solvent condition ($T<\theta$), for hydrophobic polymers, the crossover between the dilute and semidilute regime in the absence of added salt occurs at a concentration c^* given by

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

while the concentration c_b is given by

$$c_b \approx b^{-3}f(l_B/b)^{1/2}\tau^{-1/2}, \tag{39}$$

and the concentration at which beads start to overlap (concentrated regime) is given by

$$c_D \approx b^{-3}\tau. \tag{40}$$

The above concentration regimes are modified by the presence of added salt, resulting in the following expressions, now denoted by the suffix "s:" from the dilute to semidilute regime

$$c_s^* \approx c^*\left(1+\frac{2n_s}{fc_s^*}\right)^{3/2}, \tag{41}$$

which in the limit $n_s \gg c$ becomes $c_s^* \approx c^{*2/5}(2/f)^{3/5}n_s^{3/5}$; from the semidilute string-controlled to the semidilute bead-controlled regime

$$c_{bs} \approx (2n_s/f)(N^{4/5}b^{24/5}c_b^{8/5}-1)^{-1}, \tag{42}$$

while the concentration c_{Ds} remains approximately unchanged ($c_{Ds} \cong c_D$).

In the dilute regime ($c<c^*$), the relations between salt and polymer concentrations become

$$c_s^* \approx \frac{2}{f}\left(\frac{fc^*}{2}-n_s\right) \tag{43}$$

and

$$c_{bs} \approx \frac{2}{f}\left(\frac{fc_b}{2}-n_s\right). \tag{44}$$

These critical concentrations define the dilute, low-salt regime ($c<c_s^*$), dilute, high-salt string-controlled regime ($c_s^*<c<c_{bs}$), and dilute, high-salt bead-controlled regime ($c_{bs}<c<c_D$). Figure 3 shows, in a typical polyelectrolyte system, the dependence of the critical concentrations delimiting the different polyion regimes for different values of the polyion concentration c and added salt concentrations n_s.

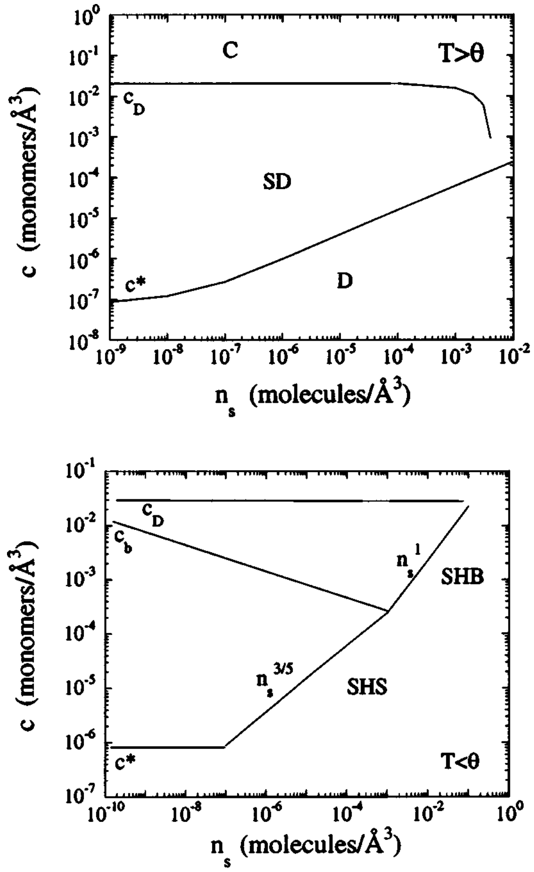

FIG. 3. Dependencies of the critical concentrations that define the different polyion regimes on the polyion concentration c and salt concentration n_s, for good solvent condition ($T>\theta$) and poor solvent condition ($T<\theta$). The concentrations are calculated with the following values: $l_B/b=2.33$, $b=3$ Å, $N=1000$, $f=0.4$ for good solvent, $T>\theta$, and $f=0.2$ and $\tau=0.8$ for poor solvent, $T<\theta$. The different concentration regimes are marked following the symbols employed by Dobrynin and Rubinstein: $T>\theta$ for D dilute regime, SD semidilute regime, and C concentrated regime; $T<\theta$ for DL dilute, low-salt regime, SLS semidilute, low-salt string-controlled regime, SLB semidilute, low-salt bead-controlled regime, SHS semidilute, high-salt string-controlled regime, SHB semidilute, and high-salt bead-controlled regime.

G. The self-diffusion coefficient ratio D_i/D_i^0

Finally, in order to calculate the electrical conductivity of the polyion solution [Eqs. (6) and (7)], the self-diffusion coefficient ratio D_i/D_i^0, according to the scaling scheme we adopted, must be evaluated. This quantity has been derived by Manning [9,10], in terms of the Fourier components of the electrostatic potential setup by the fixed polyion, according to the expression

$$\frac{D_i}{D_i^0}=1-\frac{1}{3}\sum\sum[\xi^{-1}\pi(m_1^2+m_2^2)+1]^{-2}, \tag{45}$$

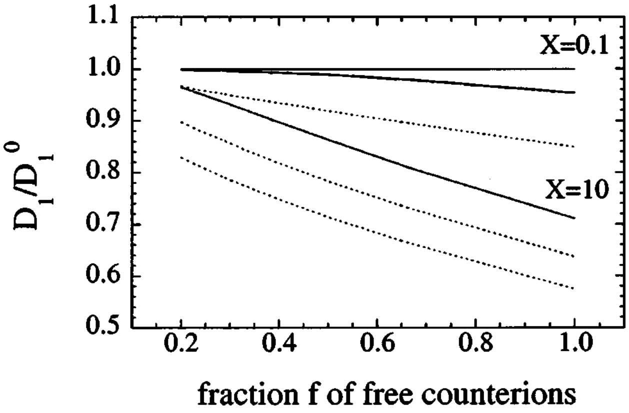

FIG. 4. Counterion self-diffusion coefficient ratio D_1/D_1^0 as a function of the fraction f of free counterions for different values of the ratio $X=c/n_s$. Full lines—good solvent condition, $T>\theta$, dilute regime; dotted lines—good solvent condition, $T>\theta$, semidilute regime.

where ξ is the charge parameter [Eq. (3)]. In the presence of added salt, for $z_1^s : z_2^s$-valent salt, polyion charged groups of valence z_p and counterions of valence z_1, the above relation becomes

$$\frac{D_i}{D_i^0}=1-\frac{1}{3}z_i^2\sum\sum z_p^2\left(\frac{\pi r_B}{l_B f g_B}(m_1^2+m_2^2)+X_s\right)^{-2}. \tag{46}$$

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

$$\frac{D_i}{D_i^0}=1-\frac{1}{3}z_i^2\sum\sum z_p^2\left(\frac{\pi\xi_0}{l_B f g}(m_1^2+m_2^2)+X_s\right)^{-2} \tag{47}$$

in the semidilute regime ($c>c^*$), respectively, where $X_s=(z_1^2+[\nu_1^s z_1^{s^2}+\nu_2^s z_2^{s^2}]n_s/fc)$. The structural parameters entering into Eqs. (46) and (47) depend on the polyion conformation, i.e., on the solvent quality parameter τ and polymer concentration c. According to the scaling approach, these parameters are given by

$$\frac{r_B}{g_B}\approx b f^{4/7}(l_B/b)^{2/7}X_s, \tag{48}$$

for $T>\theta$ and by

$$\frac{r_B}{g_B}\approx b f^{4/3}(l_B/b)^{2/3}\tau^{-1}X_s, \tag{49}$$

for $T<\theta$, in the dilute regime ($c<c^*$); and by

$$\frac{\xi_0}{g}\approx b f^{4/7}(l_B/b)^{2/7}X_s^{-1/2}, \tag{50}$$

for $T>\theta$ and by

$$\frac{\xi_0}{g}\approx b f^{4/3}(l_B/b)^{2/3}\tau^{-1}X_s^{-1/2}, \tag{51}$$

for $T<\theta$, respectively, in the semidilute regime ($c>c^*$). Figure 4 shows a typical behavior of the ratio D_1/D_1^0 as a function of the fraction of free counterions for different values of the ratio $X=c/n_s$.

III. EXPERIMENT

A. Materials

Sodium polyacrylate salts $[\text{-CH}_2\text{CH(CO}_2\text{Na)-}]_n$ (NaPAA) with nominal molecular weight 225 kD were purchased from Polysciences Inc. (Warrington, PA) as 0.25 wt/wt solutions in water. NaPAA is a water-soluble polyelectrolyte that, because of its simple chemical repeat unit, is widely used as linear charged polyion chain model. The samples were used as received without any further purification. The polymer solutions were prepared at the desired polymer concentration in the range from 10^{-6} to 10^{-2} monomol/l with deionized Q-quality water (Millipore) with an ionic conductivity lower than $(1-2)\times10^{-6}$ mho/cm at room temperature. Appropriate amounts of NaCl electrolyte solutions of known concentration have been added to the polymer solutions in order to vary, in a controlled way, the ion content. We have investigated polymer solutions at three different values of the ratio $X=c/n_s=0.1$, 1, 10, maintaining constant, for each set of measurement, the ratio between the number of monomers and the number of ions derived from the added salt.

B. Electrical conductivity measurements

The electrical conductivity of the sodium polyacrylate (NaPAA) aqueous solutions in the presence of added salt has been measured by means of frequency domain dielectric spectroscopy technique using a Hewlett-Packard Impedance Analyzer mod. 4191A in the frequency range from 1 MHz to 2 GHz. All measurements have been carried out at the temperature of 25.0 °C within 0.1 °C. At the ionic concentrations studied, the dielectric dispersion, associated with the different dielectric polarization mechanisms occurring in the whole solution induced by the polyion chain, have a dielectric strength of few dielectric units [25,26], reflecting in a conductivity dispersion within the accuracy of our experimental setup. For example, to a dielectric increment of the order of $\Delta\epsilon\approx10$, it corresponds, at frequencies of some megahertz, a conductivity increment of the order of 10^{-3} mho/m, whose influence on the frequency dependence of the conductivity is negligible. On the other hand, the orientational polarization of the aqueous phase occurs at frequencies higher than those investigated. This reflects an electrical conductivity, to a first approximation, independent of the frequency up to frequencies of few megahertz. Consequently, in the low-frequency region of the frequency interval investigated, the electrical conductivity remains constant, so that the value at the frequency of 1 MHz can be assumed as its low-frequency value (d.c. electrical conductivity).

Details of the conversion from the measured electrical impedance of the conductivity cell filled with the sample under investigation and its electrical conductivity σ have been reported elsewhere [27,28]. The overall accuracy in the range of the conductivities investigated is lower than 0.5%.

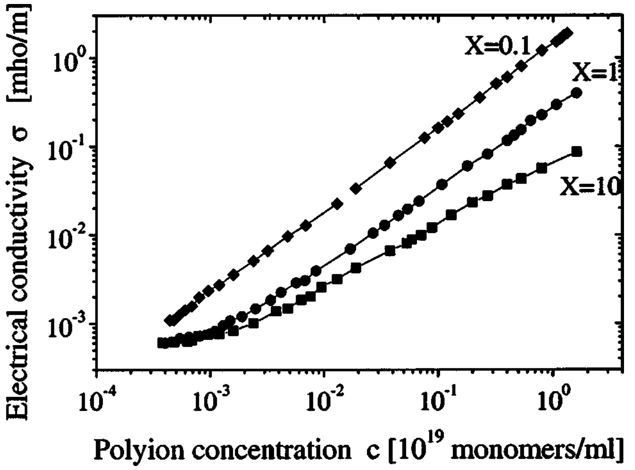

FIG. 5. The low-frequency electrical conductivity σ_0 of NaPAA aqueous solution in the presence of added salt as a function of the polyion concentration, for three different values of the ratio X: (♦)—$X=0.1$; (●)—$X=1$; (■)—$X=10$. Measurements have been carried out at the temperature of 25 °C within 0.1 °C.

C. Electrical conductivity behavior of NaPPA

The low-frequency electrical conductivity σ of NaPPA aqueous solutions in the presence of added salt at three different values of the ratio $X=c/n_s$, in a wide polyion concentration range, is shown in Fig. 5.

Typical conductivity spectra of NaPAA aqueous solution in the frequency range investigated are shown in Fig. 6. Our measurements extend in the low-frequency region of the dipolar relaxation of the aqueous phase, i.e., well below the relaxation frequency ν_{H_2O} at which the orientational relaxation of the water molecules occurs ($\nu_{H_2O}\approx 17$ GHz at room temperature [29]). In this frequency range ($\nu<\nu_{H_2O}$), the electrical conductivity $\sigma(\omega)$ shows a power law dependence on the angular frequency ω given by

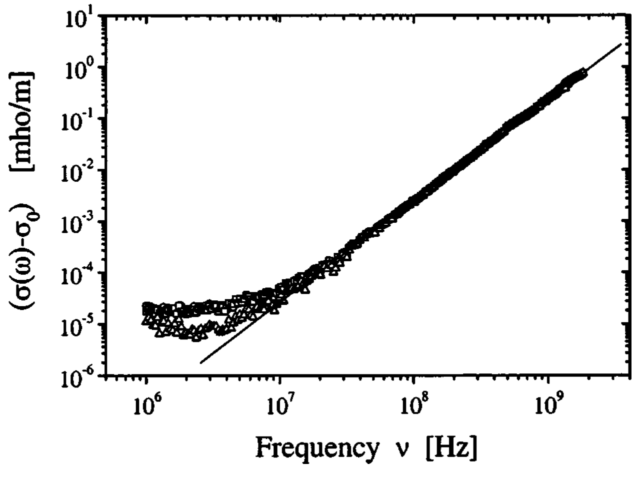

FIG. 6. The frequency dependence of the scaled electrical conductivity $[\sigma(\omega)=\sigma_0]$ of NaPAA aqueous solutions in the presence of added salt, for the three different values of the ratio X. (○)—$X=10$; (△)—$X=1$; (□)—$X=0.1$. The polyion concentration is $c=1.2\times10^{-16}$ monomer/ml.

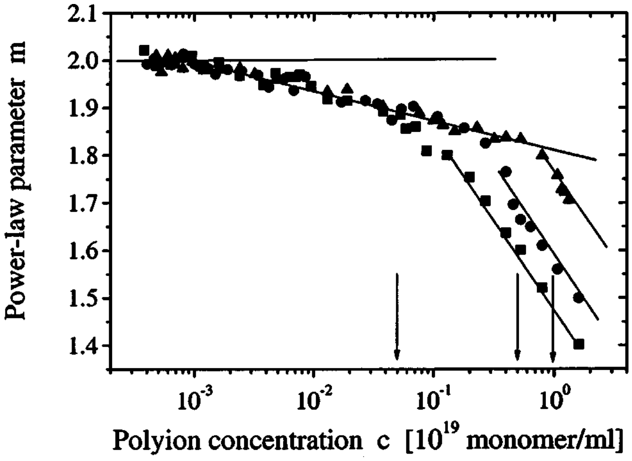

FIG. 7. The exponent m of the scaling law equation (52) for NaPAA aqueous solutions as a function of the polymer concentration, for three different values of the ratio X: (▲)—$X=0.1$; (●)—$X=1$; (■)—$X=10$. The arrows mark the concentration from dilute to semidilute regime that progressively increases with the salt concentration, from $X=10$ to $X=1$.

$$\sigma(\omega)-\sigma_0\approx\omega^m, \tag{52}$$

where σ_0 is the low-frequency limit of $\sigma(\omega)$. The exponent m has been recently related to intermolecular interactions giving rise, for example, in the glass transition, to large scale motions of various units of different polymer chains. From a phenomenological point of view, this parameter is an index of changes of the orientational organization of the water molecule dipole moment, due to the polymer-aqueous phase interactions. The exponent m, derived from a nonlinear least-squares fitting of Eq. (52) to the experimental data is shown in Fig. 7 as a function of the polymer concentration, for the three different values of the ratio X investigated. As can be seen, this parameter undergoes different regimes, depending on the polyion concentration c. Assuming that the dielectric (or conductometric) relaxation process is described by a Cole-Cole relaxation function, the electrical conductivity $\sigma(\omega)$ can be written, to a first approximation, as

$$\sigma(\omega)=\sigma_0+\omega\epsilon_0\epsilon''_{diel}\approx\omega^{2-\alpha}, \tag{53}$$

where ϵ''_{diel} is the dielectric loss and α the Cole-Cole parameter indicating the spread of the relaxation frequencies around the mean relaxation frequency of the process. Equation (53) reduces to the power law of Eq. (52) with $m=2$ ($\alpha=0$) for a Debye function, describing a single relaxation frequency process (for pure water, dielectric and conductometric dispersions are generally very well described with $\alpha\simeq 0.02$ [29]). Values of m less than 2 correspond to dispersion curves flatter than the Debye curve. As can be seen in Fig. 7, at very low polyion concentration (and consequently, at low-salt content), m approaches the value of 2, indicating that polyions do not interact (very dilute solution). As the concentration is increased, the exponent m progressively decreases indicating an increase of the polymer-solvent interactions that dramatically increase at certain polymer concentrations. We observe a change at polymer concentrations of

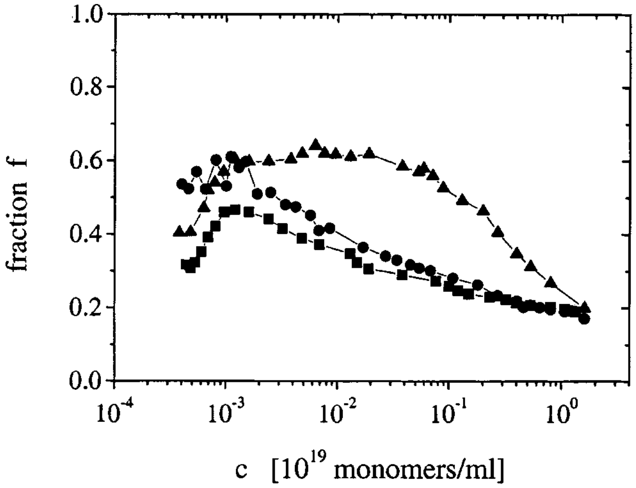

FIG. 8. The fraction *f* of free counterions in NaPAA aqueous solutions as a function of polymer concentration in the presence of added salt. (■)—$X=0.1$; (●)—$X=1$; (▲)—$X=10$.

about 5×10^{17}, of 6×10^{18}, and 1×10^{19} monomers/ml, for $X=10$, $X=1$, $X=0.1$, respectively, corresponding for these solutions containing different salt amount to the transition from the dilute to semidilute regime. It is noteworthy that these concentrations agree with those derived from Eqs. (36) and (43), based on the scaling argument (see Sec. IV). This finding suggests that the parameter *m*, indicating deviation from a single Debye-type dielectric and conductometric dispersion, probes the different concentration regimes experienced by the solution.

IV. COMPARISON WITH EXPERIMENTS

We have previously verified, by means of radiowave dielectric relaxation measurements [25], that in the case of NaPAA in aqueous solution, good solvent conditions apply. Therefore, we discuss this case in detail, whereas poor solvent conditions in appropriate polymer solutions will be treated in a forthcoming paper [30].

In order to compare the model predictions with the experimental results, we must define the concentration regimes the system experiences. In the absence of added salt, we have evaluated $c^*\approx5\times10^{-4}$ monomol/l and $c_D\approx1$ monomol/l these values being also in agreement with viscosity measurements [15]. In the presence of added salt, these concentrations shift towards higher values, according to Eqs. (36) and (37). Since each series of conductivity measurements has been carried out maintaining the ratio *X* constant, the salt concentration increases proportional to the polymer content.

The electrical conductivity model discussed above, both in the dilute and semidilute regime, depends on a single free parameter, the fraction *f* of free counterions. Figure 8 shows this parameter as a function of the polymer concentration *c*, for the three values of the ratio *X*, derived from Eq. (17) together with Eqs. (22)–(24) and from Eq. (17) together with Eqs. (25)–(27) (dilute and semidilute regime, respectively) on the basis of a nonlinear least-squares fitting procedure. The fraction *f*, for all the three values of the ratio *X* investigated, shows a marked increase with the polymer concentration, followed by an approximately constant value and then a pronounced decrease, at higher polyion concentration. This behavior (a nonmonotonic fraction of condensed counterions in good solvent condition) is qualitatively similar to that observed for the same polymer in the absence of added salt [15]. A dependence of the fraction of free counterions on the polymer concentration, i.e., a dependence of the effective charge of the polyion chain on the polymer concentration, is unexpected within the Manning model that predicts, for a linear, infinite continuously charged rigid polymer in the limit of infinite dilution a fraction of free counterion given by the value of the charge parameter ξ [Eq. (3)]. This finding clearly shows 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 flexible polyelectrolytes. At finite, relatively high polymer concentration, the presence of other chain and the flexibility effect are expected to affect the amount and the distribution of condensed counterions. The observed peculiar dependence of the fraction *f* on the polyion concentration is particularly intriguing when compared with the expected behavior in the case of hydrophobic polyelectrolytes where molecular dynamic simulations [22] have suggested that to a more compact conformation of the single chain it corresponds a strong counterion condensation effect. As pointed out by Dobrynin and Rubinstein [20], for hydrophobic polyelectrolytes, an increase of the counterion condensation is expected by increasing the polymer concentration (or by decreasing the quality of the solvent). Our findings, qualitatively in agreement with the above stated picture at the higher concentrations, show, in the case of hydrophilic polyions, a more complex behavior, suggesting that the polymer concentration might influence the counterion condensation by two different effects, i.e., an decrease of ion condensation induced by the approaching of extended polymer chains, at moderate concentration, and an increase of ion condensation as the chain assumes a more compact conformation. At higher polymer concentrations, polyelectrolyte chains interpenetrate forming a domain with a finite (constant) fraction of counterions inside it. A thermodynamic analysis of ion condensation in dilute polyelectrolyte solutions, although in the absence of added salt, has recently proved that the fraction of condensed counterions in collapsed chain conformations increases considerably [31].

With the values of *f* shown in Fig. 8, we can determine the behavior of λ_p as a function of the polyion concentration *c*, calculated from the experimental values of the conductivity σ_0 and we can compare these values with those calculated on the basis of the above scaling model in the case of good solvent condition, for the dilute and semidilute regime. This comparison is shown in Figs. 9–11. As can be seen, the agreement is rather good, for all the experiments we have done. When the solution is in dilute regime for the whole concentration range investigated (high-salt content, $X=0.1$, Fig. 9), the equivalent polyion conductance evaluated from the experimental results is well accounted for by Eqs. (17) and (22)–(24). The scatter of the experimental values in the low concentration region is due to the limited accuracy of the

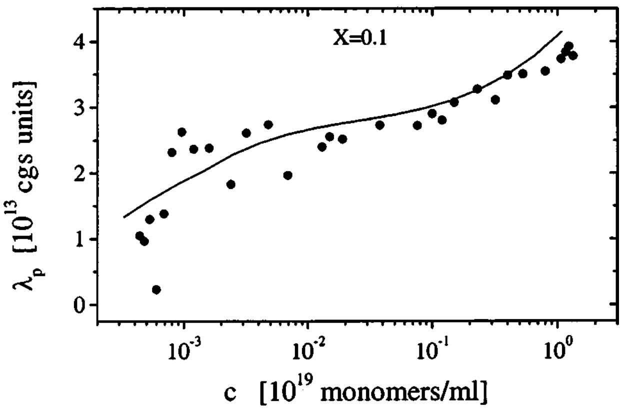

FIG. 9. Polyion equivalent conductance λ_p as a function of polymer concentration *c*, in the presence of added salt for the ratio $X=0.1$. In this concentration range, the solution is in the dilute regime. The continuous line is the calculated value, Eq. (17) together with Eqs. (22)–(24), with values of *f* given in Fig. 8.

experimental setup when we have to subtract the bulk ionic conductivity to that of the polymer solution, in salt excess condition. At $X=1$, when the influence of the added salt is relatively reduced, we expect a transition from the dilute to semidilute regime at concentrations of the order of $(5-6)\times10^{18}$ monomer/ml (corresponding to a concentration of 10^{-2} monomol/l). As can be seen in Fig. 10, the equivalent polyion conductance follows the behavior expected from Eq. (17) in the dilute regime, deviations occur just at the above stated transition concentration, approaching the value expected for semidilute condition. This trend is further confirmed in the case of $X=10$ (low-salt content, Fig. 11), where the transition between the dilute and semidilute regime occurs at concentration of the order of 5×10^{17} monomers/ml (corresponding to a concentration of 8×10^{-4} monomol/l).

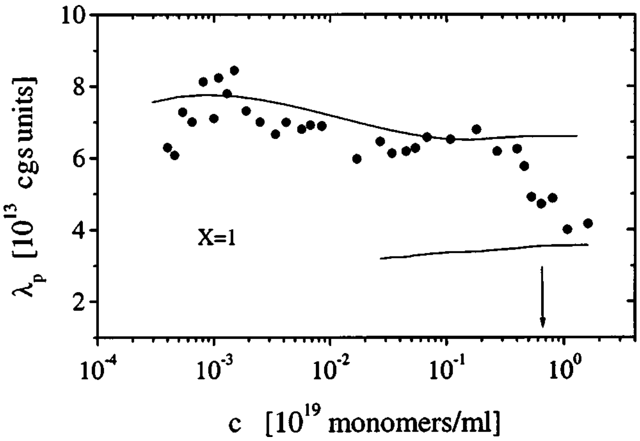

FIG. 10. Polyion equivalent conductance λ_p as a function of polymer concentration *c*, in the presence of added salt for the ratio $X=1$. The arrow marks the transition from the dilute to semidilute regime. The continuous lines are the calculated values of λ_p in the dilute regime (upper curve) and in the semidilute regime (lower curve) with the values of *f* given in Fig. 8. The arrow marks the transition from the dilute to semidilute regime.

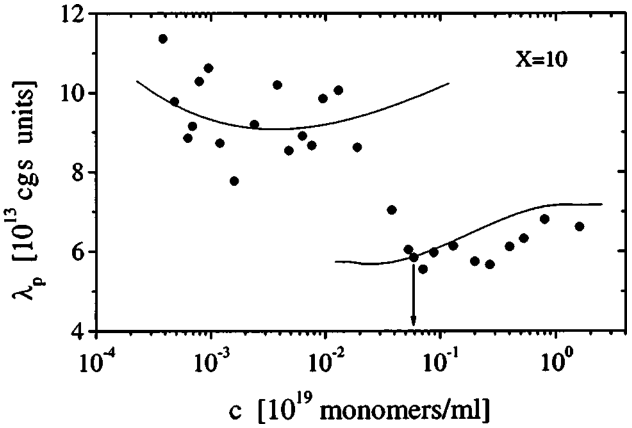

FIG. 11. Polyion equivalent conductance λ_p as a function of polymer concentration *c*, in the presence of added salt for the ratio $X=10$. The arrow marks the transition from the dilute to semidilute regime. The continuous lines are the calculated values of λ_p in the dilute regime (upper curve) and semidilute regime (lower curve) with the values of *f* given in Fig. 8. The arrow marks the transition from the dilute to semidilute regime.

V. CONCLUSIONS

In this paper, we have used the scaling approach proposed by Dobrynin, Colby, and Rubinstein [12] and by Dobrynin and Rubinstein [13] to describe the electrical conductivity properties of a polyelectrolyte solution in the presence of added salt in a good solvent condition. Either in the dilute or semidilute regime, where the presence of added salt causes the polymer chain to behave as a random walk of correlation blobs, the polyion equivalent conductance has been calculated along the line proposed by Manning and has been compared with that measured for a polyion in the presence of added salt (NaPAA aqueous solutions at different NaCl salt concentrations). The agreement is rather good over the whole concentration range investigated, giving a strong evidence for the correctness of the scaling approach in order to analyze the transport properties of an ionic solution.

Our measurements also suggest a relation between the counterion condensation and polyion concentration, different from that predicted by the Manning model for linear rigid polyion chain in the limit of infinite dilution. In particular, we suggest that the effective charge on the polyion chain, after condensation has occurred, depends on the polymer concentration, i.e., the distribution of free counterions is influenced by the presence of other chains and by the conformation they assume. The gradual increase of counterion condensation as the polymer concentration increases in the semidilute regime plays an important role to explain the behavior of polyelectrolyte solution in good solvent condition.

Finally, we suggest that conductivity measurements could provide reliable evidence (or a direct proof) for the existence of necklace conformation of a polyelectrolyte chain under poor solvent conditions, giving an effective picture of the influence of the solvent quality parameter and the conformation of a flexible polyelectrolyte chain. This investigation is in progress.

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