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Solvent quality influence on the dielectric properties of polyelectrolyte solutions: A scaling approach

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The dielectric properties of polyelectrolytes in solvent of different quality have been measured in an extended frequency range and the dielectric parameters associated with the polarization induced by counterion fluctuation over some peculiar polyion lengths have been evaluated. Following the scaling theory of polyelectrolyte solutions and the recent models developed by Dobrynin and Rubinstein that explicitly take into account the quality of the solvent on the polyion chain conformation, we have reviewed and summarized a set of scaling laws that describe the dielectric behavior of these systems in the dilute and semidilute regime. Moreover, for poorer solvents, where theory of hydrophobic polyelectrolytes predicts, and computer simulation confirms, a particular chain structure consisting of partially collapsed monomers (beads) connected by monomer strings, we derived a scaling law. These predictions are compared with the results obtained from the dielectric parameters (the dielectric increment $\Delta\epsilon$ and the relaxation time τ_{ion}) of the "intermediate" frequency relaxation of two partially charged polymers, which possess a carbon-based backbone for which water is a poor solvent and ethylene glycol is a good solvent. By varying the solvent composition (a water-ethylene glycol mixture), we have tuned the quality of the solvent, passing from poor to good condition and have observed the predicted scaling for all the systems investigated. These findings give a further support to the scaling theory of polyelectrolyte solutions and to the necklace model for hydrophobic polyelectrolytes in poor solvents.

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I. INTRODUCTION

Polyelectrolytes are macromolecules bearing many ionizable groups that in solution can dissociate leaving a charged polyion chain and counterions of opposite charge [1–3]. The presence of long-ranged forces of electrostatic origin imparts to these systems a very complex phenomenology, which differs from the one of the simple electrolyte solutions, where ions interact through a screened Coulomb pair potential, and from the one of uncharged polymers making these systems interesting from a fundamental point of view.

In charged polymers, the chain conformation is governed by the balance between the chain entropy and the electrostatic repulsion of the charged monomers, which leads to the formation of noticeable structures.

The scaling theory of polyelectrolyte solutions [4], based on the idea of electrostatic blobs inside which electrostatic repulsion competes with polymer-solvent interaction [5], provides an overall polymer chain conformation in the different concentration regimes, from the dilute to the semidilute entangled regime. Moreover, in poor solvent media, a pearl necklace structure forms, in which the chain collapses into compact aggregates (beads) connected by flexible chain segments (strings).

Although evidences for this pearl-necklace picture have been given by Aseyev *et al.* [6] and by Lee *et al.* [7], the overall phenomenology of these systems until now, has not been well understood. Recently, Waigh *et al.* [8], using small-angle x-ray scattering, have evidenced in polyions in polar organic solvents of different quality and polarity two distinct regimes, a string-controlled regime and a bead-controlled one, in qualitative agreement with the theory of Dobrynin *et al.* [9] and Dobrynin and Rubinstein [10,11].

Polyion chains undergo different conformations responding to change of environment, mainly the ionic strength and the solvent quality. Because of the interplay of the short-ranged attractive forces and long-ranged Coulombic forces, the charge on the polyion and the partial release of counterions into the solution drive the polyion to dissolve in solvents of high enough dielectric constant, even if the energetic interaction between uncharged monomers and solvent is unfavorable. Such solvents are referred to as "poor solvents" and the conformation of the chain is collapsed into beads in order to minimize the contact between monomers and solvent. This conformation is governed by the solvent quality parameter τ in poor solvents, where by "poor" we mean that the solvent quality is bad for the neutral chain. This parameter defines the relative temperature distance from the "theta" point, $\tau=(\theta-T)/\theta$, and θ represents the temperature at which the net excluded volume for the uncharged monomers is zero. The solvent quality parameter $\tau=0$ at $T=\theta$ and τ increases toward unity as the solvent becomes poorer ($T<\theta$).

Recently, we have investigated the electrical conductivity behavior of polyions in solvent of different quality [12] and, in particular, we have presented a theory to take into account the necklace configuration when the polyion is in a poor solvent.

In this paper, we extend these previous investigations to the dielectric properties of these systems in the light of the scaling theory of polyelectrolyte solutions. We have investigated the radiowave dielectric properties of copolymers of 2-vinyl-pyridine and N-methyl-2-vinyl pyridinium chloride,

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[PMVP-Cl], at two different charge densities, in different mixed solvents, ranging from pure water (poor solvent) to pure ethylene glycol [EG] (good solvent). The dielectric behavior of this polymer has been compared to the one of poly(2-vinyl pyridine), [P2VP], an uncharged linear polymer from which the two above polyions were made by partial random quaternization. The polymers investigated, the uncharged P2VP and the two partially charged PMVP-Cl polyions, possess a carbon-based backbone for which water is a poor solvent and for all of them ethylene glycol [EG] behaves as a good solvent [13]. Thus, in this context, one can easily transform the polymer-solvent system from poor-solvent to good-solvent conditions simply by adjusting the EG-water mixture composition. A direct observation of the complexity of the P2VP chain, when charged segments alternate with collapsed globules, has been recently reported by Minko *et al.* [14] for the polymer adsorbed onto a flat surface and by Kiriy *et al.* [15] for polymer in poor solvent (water).

The dielectric measurements presented in this work extend in a wide frequency range, from few kilohertz to some gigahertz. However, we analyze in detail only the dielectric relaxation occurring in the intermediate frequency range (100 kHz up to 100 MHz), where the molecular polarization mechanisms are associated with the counterion fluctuation along some typical polyion lengths, reflecting the polymer conformation [16]. To our knowledge, such a study has not been undertaken previously.

The paper is organized as follows. In Sec. II, we will summarize the known results on the scaling theory of hydrophobic polyelectrolytes in different solvent qualities, following the theory developed by Dobrynin *et al.* [4]. In Sec. III, we analyze the dielectric spectra and discuss the deconvolution procedure we have employed in order to derive the dielectric parameters associated with the polyion chain polarization. In Sec. IV, we present and discuss results for the dielectric properties of the polymer solutions in the semidilute regime, as the solvent quality is progressively varied from good- to poor-solvent conditions and finally in Sec. V we present a summary and some conclusions.

II. THEORETICAL BACKGROUND

In this section, we will review the main scaling relationships for polyelectrolyte chains in the case of dilute and semidilute solutions, below and above the overlap concentration c^*, in poor and good solvent conditions.

Consider a polymer chain with degree of polymerization N, monomer size b, polyion length $l=Nb$, and numerical monomer concentration c, in a solvent with dielectric constant ϵ. The polyion chains are partially charged because of their charged side groups incorporated by a quaternization procedure (see Sec. III), so that the total number of ionizable groups per chain is $N_c=QN$, where Q is the quaternized fraction of monomers.

These ionizable groups, due to the counterion condensation partially dissociate by releasing counterions in the solution and leaving ionized groups on the polymer backbone. In salt-free solutions, the number of counterions released by a chain is equal to the net charge on the polymer chain.

Each polyion bears an electric charge $Q_p=fNz_pe$ and releases in the solvent phase fN counterions, each of them with a charge z_1e. The electroneutrality condition implies $z_p=\nu_1 z_1$, with z_p and z_1 valences of the charged groups on the polyion chain and counterions and ν_1 the counterion dissociation constant, respectively. Here f is the fraction of monomers on the chain that bears an effective charge (after counterion condensation occurred) and consequently f/Q is the fraction of counterions released in the bulk solution (free counterions).

According to the Manning counterion condensation theory [17–19], the effect of counterion condensation is governed by the charge density parameter $\xi=l_B/b_{\text{eff}}=e^2/\epsilon k_B T b_{\text{eff}}$ defined as the ratio between the Bjerrum length l_B (~7 Å at 25 °C in water and ~15 Å at 25 °C in EG) and the effective average charge spacing b_{eff} between charged groups on the polymer chain. If $\xi>1$ (for univalent counterion), a fraction $(1-f)=1-1/(|z_p z_1 \xi|)$ of counterions will condense on the polyion chain to reduce its effective charge to a critical value corresponding to $\xi_p=1/|z_p z_1|$. In this paper, we consider $z_p=z_1=1$.

Following the scaling theory of polyelectrolyte solutions of Dobrynin *et al.* [4], in good solvent conditions and in the dilute regime, the polymer chain is stretched and can be represented by a directed random walk of length $L=N_D D_b$ of N_D electrostatic blods of size D_b, each of them containing g_e monomers. According to Dobrynin *et al.* [4], these quantities scale as

$$N_D \sim N f^{10/7} (l_B/b)^{5/7}, \tag{1}$$

$$D_b \sim b f^{-6/7} (l_B/b)^{-3/7}, \tag{2}$$

$$g_e \sim f^{-10/7} (l_B/b)^{-5/7}. \tag{3}$$

In the semidilute regime, the polyion is modeled as a random walk of N_{ξ_0} correlation blobs of size ξ_0, each of them containing g monomers. In good solvent conditions, the characteristic parameters scale as

$$N_{\xi_0} \sim N f^{6/7} (l_B/b)^{3/7} b^{3/2} c^{1/2}, \tag{4}$$

$$\xi_0 \sim b^{-1/2} (l_B/b)^{-1/7} f^{-2/7} c^{-1/2}, \tag{5}$$

$$g \sim b^{-3/2} (l_B/b)^{-3/7} f^{-6/7} c^{-1/2}. \tag{6}$$

In poor solvent conditions, where a competition between the solvent quality and the electrostatic repulsion arises, the characteristic parameters scale as

$$N_{\xi_0} \sim N f^2 (l_B/b) b^{3/2} \tau^{-3/2} c^{1/2}, \tag{7}$$

$$\xi_0 \sim b^{-1/2} (l_B/b)^{-1/3} f^{-2/3} \tau^{1/2} c^{-1/2}, \tag{8}$$

$$g \sim b^{-3/2} (l_B/b)^{-1} \tau^{3/2} f^{-2} c^{-1/2}. \tag{9}$$

Both theory [9–11] and simulation [20–22] suggest that, in poor solvent conditions, the local conformation of polyion can be more interesting than the above stated electrostatic blob picture and regions of strong local collapse can appear (the pearl-necklace model). Dobrynin *et al.* [9] have developed a scaling theory, both in the dilute and in the semidilute regime, in which the standard rodlike conformation is abandoned in favor of a necklace structure where each blob, because of a competition between surface tension effects and electrostatic interactions, in analogy with the shape instability of a charged droplet, splits into a set of small charged globules (beads) connected by long and narrow strings. Following the derivation given by Dobrynin *et al.* [9] and Dobrynin and Rubinstein [10,11], when the polyion effective charge becomes larger than a critical value, 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 chain is $L_{\mathrm{nec}}=N_b l_s$, since the most length is stored in the strings ($l_s > D_b$).

Moreover, in the semidilute regime ($c>c^*$), a new characteristic concentration c_b appears, which defines two different concentration regimes. In the string-controlled regime ($c^*<c<c_b$), the chain is assumed to be a random walk of $N_{\xi_0}=N/g_{\xi_0}$ correlation segments of size ξ_0, each of them containing g_{ξ_0} monomers. The correlation length is much larger than the size of the bead and the chain is predicted to have a bead-necklace structure on length scales smaller than the correlation length [23]. On longer length scales, the chain obeys ideal random walk statistics and the size of the chain is

$$R \sim \xi_0\left(\frac{N}{g_{\xi_0}}\right)^{1/2} \sim bN^{1/2}(c_b/c)^{1/4}. \tag{10}$$

In the bead-controlled regime ($c_b<c<c_D$), this model predicts only one bead per correlation blob of size ξ_0, containing $g_{\xi_0}=\tau(l_B/b)^{-1}f^{-2}$ monomers. The correlation length is of the order of the size of the bead and the chains are predicted to have a bead structure on length scales smaller than the correlation length [23]. The chain size is

$$R \sim \xi_0\left(\frac{N}{g_{\xi_0}}\right)^{1/2} \sim bN^{1/2}(c_b/c)^{1/3}. \tag{11}$$

The scaling theory predicts the dependencies of the characteristic parameters of the model. Here, we give only a short overview of the most relevant results of the scaling theory for the necklace regime of hydrophobic polyelectrolytes. In the dilute regime ($c<c^*$), the number of beads N_b, the size of beads D_b, and the length of strings l_s scale as

$$N_b \sim N/g_b \sim N(l_B/b)\tau^{-1}f^2, \tag{12}$$

$$D_b \sim b(l_B/b)^{-1/3}f^{-2/3}, \tag{13}$$

$$l_s \sim b(l_B/b)^{-1/2}f^{-1}\tau^{1/2}. \tag{14}$$

In the semidilute regime, the following relationships hold: In the string-controlled regime ($c^*<c<c_b$)

$$\xi_0 \sim b^{-1/2}\tau^{1/4}(l_B/b)^{-1/4}f^{-1/2}c^{-1/2}, \tag{15}$$

$$g_{\xi_0} \sim b^{-3/2}\tau^{3/4}(l_B/b)^{-3/4}f^{-3/2}c^{-1/2}, \tag{16}$$

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

$$\xi_0 \sim \tau^{1/3}(l_B/b)^{-1/3}f^{-2/3}c^{-1/3}, \tag{17}$$

$$g_{\xi_0} \sim \tau(l_B/b)^{-1}f^{-2}. \tag{18}$$

In all the above expressions, we dropped numerical coefficients (of the order of unity) to keep the discussion at the scaling level.

Although some features of the necklace picture have been confirmed by computer simulations [21,24] performed in different conditions, by using Debye-Hückel approximation or full Coulombic interactions [20,22], there is, up to now, no clear experimental evidences for the existence of a necklace chain, even if some properties consistent with the necklace model have been observed [8,12,25,26].

A. Scaling in the framework of the Ito model (Refs. [16,27])

The dielectric relaxation considered in this work, intermediate between the one where the polarization due to the whole polyion length dominates and the one where the relaxation of the pure solvent occurs, results from the counterion polarization along a length scale of the order of the correlation length. According to Ito *et al.* [27], in the dilute regime ($c<c^*$), free counterions can polarize by free diffusion [in a three-dimensional (3D) space] to a scale of the order of the distance between chains R_{cm}

$$\tau_{\mathrm{ion}} \sim \frac{R_{\mathrm{cm}}^2}{6D} \tag{19}$$

and the dielectric increment $\Delta\epsilon$ is simply the product of the number density of free counterions, cf, and their polarizability α_{ion} which is determined by the square of the ion charge (e for univalent counterions) and the polarization distance R_{cm}

$$\Delta\epsilon \sim fc\alpha_{\mathrm{ion}} \sim fc\frac{e^2R_{\mathrm{cm}}^2}{k_BT} \sim fc\,\epsilon\, l_B R_{\mathrm{cm}}^2. \tag{20}$$

In the semidilute regime ($c>c^*$), free counterions can polarize by simple diffusion within the correlation volume ξ_0^3. In this case, the relaxation time τ_{ion} is the time required to diffuse a distance of the order of the correlation length ξ_0

$$\tau_{\mathrm{ion}} \sim \frac{\xi_0^2}{6D} \tag{21}$$

and the dielectric increment $\Delta\epsilon$ is once again the product of the number density (numerical concentration), fc, of free counterions and their polarizability $\alpha_{\mathrm{ion}} \sim (e\xi_0)^2/k_BT$

$$\Delta\epsilon \sim fc\alpha_{\mathrm{ion}} \sim fc\frac{e^2\xi_0^2}{k_BT} \sim fc\,\epsilon\, l_B\xi_0^2. \tag{22}$$

It is worth noting that the fraction f of monomers bearing an effective charge can be obtained by either combining Eqs. (19) and (20) in the dilute regime or Eqs. (21) and (22) in the semidilute regime, resulting in the expression

$$f \sim \frac{\Delta\epsilon}{6D\tau_{\mathrm{ion}} l_B \epsilon c}. \qquad (23)$$

In the dilute regime, for any solvent quality, the distance between chains scales with the concentration c according to

$$R_{\mathrm{cm}} \sim \left(\frac{N}{c}\right)^{1/3} \qquad (24)$$

resulting in a relaxation time τ_{ion} and in a dielectric increment $\Delta\epsilon$ given by

$$\tau_{\mathrm{ion}} \sim N^{2/3} c^{-2/3}, \qquad (25)$$

$$\Delta\epsilon \sim f N^{2/3} c^{1/3}. \qquad (26)$$

Conversely, in the semidilute regime, the correlation length ξ_0 depends on the solvent quality. In good solvent condition

$$\xi_0 \sim f^{-2/7} c^{-1/2} \qquad (27)$$

and in poor solvent condition

$$\xi_0 \sim f^{-2/3} c^{-1/2} \tau^{1/2}. \qquad (28)$$

These dependencies result in the following scaling relationships:

$$\tau_{\mathrm{ion}} \sim f^{-4/7} c^{-1}, \qquad (29)$$

$$\Delta\epsilon \sim f^{3/7}, \qquad (30)$$

in good solvent condition and in the following scaling relationships:

$$\tau_{\mathrm{ion}} \sim \tau f^{-4/3} c^{-1}, \qquad (31)$$

$$\Delta\epsilon \sim \tau f^{-1/3}, \qquad (32)$$

in poor solvent condition. Combining Eqs. (29) and (30) with Eq. (23) or Eqs. (31) and (32) with Eq. (23) determines the scaling behavior of the overall dielectric properties, i.e.,

$$\Delta\epsilon^{-4/3} \tau_{\mathrm{ion}}^{-1} \sim c \qquad (33)$$

in good solvent condition and

$$\Delta\epsilon^{4/3} \tau^{-1} \tau_{\mathrm{ion}}^{-1/3} \sim c^{1/3} \qquad (34)$$

in poor solvent condition, respectively.

Within the pearl necklace model, for most of our purposes, its details are not essential, since this model maps the beads and strings (or whatever other local conformations) onto a cylinder of appropriate diameter. However, in analogy with the above stated scaling laws, according to the basic Eqs. (21) and (22), fluctuation of free counterions over distance of the order of the correlation length $\xi_0 \sim f^{-1/2} c^{-1/2} \tau^{1/4}$ [Eq. (15)], results in a scaling law given by

$$\Delta\epsilon \tau_{\mathrm{ion}} \sim f c \xi_0^4 \sim \tau f^{-1} c^{-1}. \qquad (35)$$

It is worth noting that Eq. (35) differs from the one derived directly from Eqs. (19) and (20) in dilute regime, or from Eqs. (21) and (22) in the semidilute regime, following the Ito *et al.* model [27]. In this case, the characteristic dependence of ξ_0 for the semidilute, string-controlled regime, has been directly substituted in the expressions for $\Delta\epsilon$ and τ_{ion}. This means that $\Delta\epsilon \sim \tau^{1/2}$ and $\tau_{\mathrm{ion}} \sim f^{-1} c^{-1} \tau^{1/2}$. Both the two above dependencies are summarized in the scaling expression (35).

III. EXPERIMENT

A. Materials

Poly(2-vinyl-pyridine), [P2VP], (M_w=364 kD) was purchased from Polymer Source Inc. (Montreal, Canada) and was used without further purification. The polyion of poly (N-methyl-2-vinyl pyridinium chloride), [PMVP-Cl], were prepared from the neutral parent dry polymer P2VP by means of a quaternization procedure. P2VP dissolved in N-dimethyl formamide [DMF] was quaternized with dimethyl sulfate (on the pyridine nitrogen) and the methyl sulfate counteranion was substituted by Cl^- upon addition of NaCl. By means of this procedure, two different samples with two different degrees of quaternization (Q=0.17 and Q=0.55) were prepared. The polydispersity index of the samples is estimated to be M_w/M_n=1.06 and the degree of quaternization Q of the partially quaternized polymers was determined by using sodium chloride and silver nitrate based on the standard counterion titration technique.

We employed as solvent mixed ethylene glycol-water solutions at five different molar fractions $X=[EG]/([EG]+[H_2O])$ (X=0, 0.25, 0.50, 0.75, 1). The polymer concentration was varied in the range from 0.01 to 10 mg/ml; this range covering the dilute and the semidilute regime. All the dilutions were prepared using deionized Q-quality water (electrical conductivity σ less than 1×10^{-6} mho/cm, at room temperature) and highly purified grade ethylene glycol (Sigma Chem. Co., St. Louis, MO). All the dielectric measurements were done at the temperature of 25.0±0.1 °C.

B. Dielectric measurements

The dielectric and conductometric spectra of uncharged P2VP and partially charged PMVP-Cl polymers have been measured in the frequency range from 1 kHz to 2 GHz by means of two radio-frequency Impedance Analyzers, Hewlett-Packard model 4294A (in the frequency range from 1 kHz to 10 MHz) and model 4291A (in the frequency range from 1 MHz to 2 GHz). Details of the dielectric cell and the calibration procedure have been reported elsewhere (Refs. [28,29]).

C. Analysis of the dielectric spectra

Representative dielectric and conductometric spectra of 55%PVMP-Cl aqueous solutions at some selected polymer concentrations are shown in Figs. 1 and 2. All the polymer solutions investigated display a well-defined dielectric dispersion with relaxation time falling in the interval 10^{-6}–10^{-8} s, intermediate between the low-frequency dispersion associated with the counterion fluctuation along the whole polymer chain and the high-frequency dispersion due to the orientational polarization of the aqueous phase. In the frequency range investigated, the complex dielectric constant

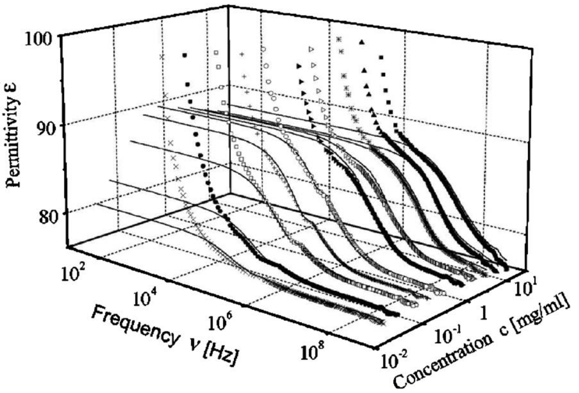

FIG. 1. Typical dielectric spectra of 55%PMVP-Cl in water (poor solvent) at some selected polyion concentrations: (×): 0.015 mg/ml (●): 0.030 mg/ml; (□): 0.080 mg/ml; (+): 0.15 mg/ml; (○): 0.30 mg/ml; (▼): 0.80 mg/ml; (▽): 1.50 mg/ml; (*): 3.03 mg/ml; (▲): 6.0 mg/ml; (■): 10.0 mg/ml. The temperature is 25.0±0.1 °C. The full lines are the calculated values from the fitting procedure employed, according to Eq. (36).

$\epsilon^*(\omega)$ has been analyzed [30] by the superposition of a Cole-Cole relaxation function and a Debye relaxation function which models the orientational polarization of the solvent phase, in the higher frequency range

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\frac{\sigma(\omega)}{\epsilon_0\omega} = \epsilon'(\omega) - i\left(\epsilon''_{\text{diel}}(\omega) + \frac{\sigma_0}{\epsilon_0\omega}\right) = \frac{\epsilon - \epsilon_\infty}{1 + (i\omega\tau_{\text{ion}})^\beta} + \frac{\epsilon_\infty - \epsilon_{\infty\text{H}_2\text{O}}}{1 + i\omega\tau_{\text{H}_2\text{O}}} - i\frac{\sigma_0}{\epsilon_0\omega}, \quad (36)$$

where $\Delta\epsilon = \epsilon - \epsilon_\infty$, $\nu_{\text{ion}} = 1/2\pi\tau_{\text{ion}}$, and β (the dielectric strength, relaxation frequency, and relaxation time spread, respectively) are the dielectric parameters associated with the polyion relaxation and $\Delta\epsilon_{\text{H}_2\text{O}} = \epsilon_\infty - \epsilon_{\infty\text{H}_2\text{O}}$, $\nu_{\text{H}_2\text{O}} = 1/2\pi\tau_{\text{H}_2\text{O}}$ are the dielectric parameters (dielectric strength and relaxation frequency, respectively) associated with the solvent phase. At the temperature of 25 °C, these quantities are $\Delta\epsilon_{\text{H}_2\text{O}} = 78.5$ and $\tau_{\text{H}_2\text{O}} = 8.75$ ps [31]. σ_0 is the dc electrical conductivity and, finally, ϵ_0 the dielectric constant of free space and ω the angular frequency of the applied electric field.

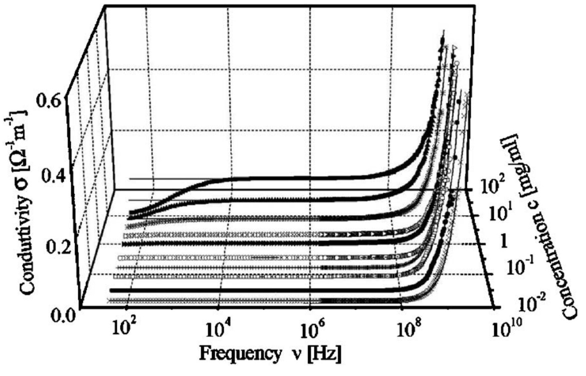

FIG. 2. Typical conductivity spectra of 55%PMVP-Cl in water (poor solvent) at some selected polyion concentrations: (×): 0.015 mg/ml; (●): 0.030 mg/ml; (□): 0.080 mg/ml; (+): 0.15 mg/ml; (○): 0.30 mg/ml; (▼): 0.80 mg/ml; (▽): 1.50 mg/ml; (*): 3.03 mg/ml; (▲): 6.0 mg/ml; (■): 10.0 mg/ml. The temperature is 25.0±0.1 °C. The full lines are the calculated values from the fitting procedure employed, according to Eq. (36).

As can be seen in Figs. 1 and 2, in the low-frequency region of the frequency interval investigated, a further contribution, associated with the electrode polarization effect, dominates. The deconvolution of a dielectric spectrum covering an extended frequency range, where different relaxation mechanisms overlap, is a very difficult task. This difficulty is particularly hard when the electrical conductivity of the samples to be studied gives rise to a frequency-dependent loss process falling within the frequency window investigated. In the presence of an electrode polarization contribution, depending on the dc electrical conductivity σ_0 of the samples investigated, a constant phase angle (CPA) element has been used to describe the frequency response of the electrode-solution interface. The "overall" complex dielectric constant has been written as the sum of two contributions

$$\epsilon^*_{\text{tot}}(\omega) = A(i\omega)^{-\gamma} + \epsilon^*(\omega). \quad (37)$$

The parameters A and γ have been derived from the low-frequency region of the spectra, where the electrode polarization contribution exceeds by orders of magnitude the effects associated with the polyion and follows a well-defined power-law. Details to reduce the contribution of electrode polarization effects in the radiowave dielectric measurements of conductive solutions are reported elsewhere [29].

As we have previously stated, the deconvolution of the whole dielectric spectrum into its components in the case of highly conductivity aqueous solutions is very difficult. In the present case, more complicated by the fact that, due to the conductivity, the experimental resolution is low and that, in our frequency window, we can observe only the high-frequency tail of the dc conductivity losses and only the low-frequency tail of the aqueous phase polarization.

In particular, the localization of the intermediate frequency relaxation by observing separately the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''_{\text{diel}}(\omega) = [\sigma(\omega) - \sigma_0]/(\epsilon_0\omega)$ spectra may be doubtful, thus influencing the evaluation of the whole set of the dielectric parameters. To overcome this difficulty, we have performed a multiple-step fitting procedure based on the Marquardt algorithm for complex functions [32]. Since the shape of the dielectric loss spectrum ϵ''_{diel} strongly depends on the value of the dc electrical conductivity σ_0 to be subtracted from the total loss $\sigma(\omega)/\epsilon_0\omega$, we have made a preliminary simultaneous fit of $\epsilon'(\omega)$ and the total loss $\sigma(\omega)/\epsilon_0\omega$ with five free parameters $\Delta\epsilon$, τ_{ion}, β, ϵ_∞, σ_0 with the only constraint that all parameters should be >0. The value of σ_0 thus obtained is then subtracted from the measured conductivity $\sigma(\omega)$, the dielectric loss $\epsilon''_{\text{diel}}(\omega)$ is evaluated and a new set of parameters from the simultaneous fit of both the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''_{\text{diel}}(\omega)$ are now obtained. This procedure is iterated until a reasonable minimization is reached and the dielectric parameters $\Delta\epsilon$ and τ_{ion} converge to stable values. It is worth noting that the same set of parameters describe both the real part, the permittivity ϵ', and the imaginary part $\epsilon''_{\rm diel}$ of the complex dielectric constant. This circumstance gives a strong support to the reliability of the dielectric data we present. A further check of the goodness of the fit we performed can be found in the values we obtain for the parameters σ_0 and ϵ_∞. Their values, within the derived uncertainties, agree with the values measured directly in the high-frequency limit for ϵ_∞ and in the low-frequency limit for σ_0. Even if the fitting algorithm works with five free parameters, actually their number is reduced to three ($\Delta\epsilon$, $\tau_{\rm ion}$, and β). The uncertainties derived from the nonlinear least-squares minimization vary between 2 and 5 % for $\Delta\epsilon$ and between 5 and 8 % for $\tau_{\rm ion}$, according to the quality of the solvent and the polyion concentration. In pure ethylene glycol, at the lowest polymer concentration employed, the dielectric strength is less than 1–2 dielectric units and the uncertainties on the dielectric parameters are appreciably larger. As an example, in the most favorable case (55%PMVP-Cl in water, $C=10$ mg/ml), the set of the dielectric parameters derived from the fitting procedure is $\Delta\epsilon=12.5\pm0.1$, $\nu_{\rm ion}=46\pm2$ MHz, $\epsilon_\infty=77.5\pm0.3$, and $\beta=0.26\pm0.02$.

To judge the goodness of the overall procedure we used, Fig. 3 shows a typical dielectric spectrum, in the case of 55%PMVP-Cl polyion in water, together with a Cole-Cole plot $[\epsilon''_{\rm diel}(\omega),\epsilon'(\omega)]$ where the intermediate relaxation investigated in this work is well evidenced and well separated from the electrode polarization effect (deviation from the Cole-Cole arc at the right side) and the orientational relaxation of the aqueous phase (deviations from the Cole-Cole arc at the left side). As can be seen, the calculated values on the basis of Eq. (36) give a reasonable agreement with the experimental data (in the frequency range over the intermediate relaxation dominates, the correlation coefficient is better than $R=0.999\,87$) and, moreover, allow the dielectric parameters $\Delta\epsilon$ and $\tau_{\rm ion}$ to be determined with a reasonable accuracy.

IV. RESULTS AND DISCUSSION

For the polymers with degree of quaternization $Q=0.55$, the charge density parameter ξ spans between $\xi=l_B/b_{\rm eff}\simeq1.3$ for pure water and $\xi=l_B/b_{\rm eff}\simeq2.7$ for pure ethylene glycol and consequently counterion condensation is expected. As pointed out by Waigh *et al.* [8], in the poor solvent case, counterion condensation is more complex than the Manning theory predicts, since condensation can take place on strings, on beads, and on the whole necklace chain, with an extent controlled by the charge density on the different structures. However, the presence of a fraction of free counterions originates the "intermediate" frequency dielectric relaxation we have observed. The dielectric behavior of 55%PMVP-Cl as a function of the polymer concentration C, expressed in mg/ml is shown in Figs. 4 and 5, where the data are plotted according to the scaling relationships (33) and (34), which apply in the case of good- and poor-solvent conditions, respectively. The data clearly show where the semidilute regime holds. Deviations from the semidilute power law (straight line behavior) occur at polymer concentrations lower than the overlap concentration c^* (marked by the arrows in Figs. 4 and 5). Recently, two of us (S.D. and R.H.C.) have measured the rheology properties of these polymers, both in water and in ethylene glycol, and have determined the overlap concentration c^* as the concentration at which the specific viscosity $\eta_{sp}=(\eta-\eta_s)/\eta_s$, where η and η_s are the zero shear viscosity of the solution and the solvent, respectively, is approximately unity. This concentration is $c^*=0.05$ mg/ml for polymer in water and $c^*=0.25$ mg/ml for

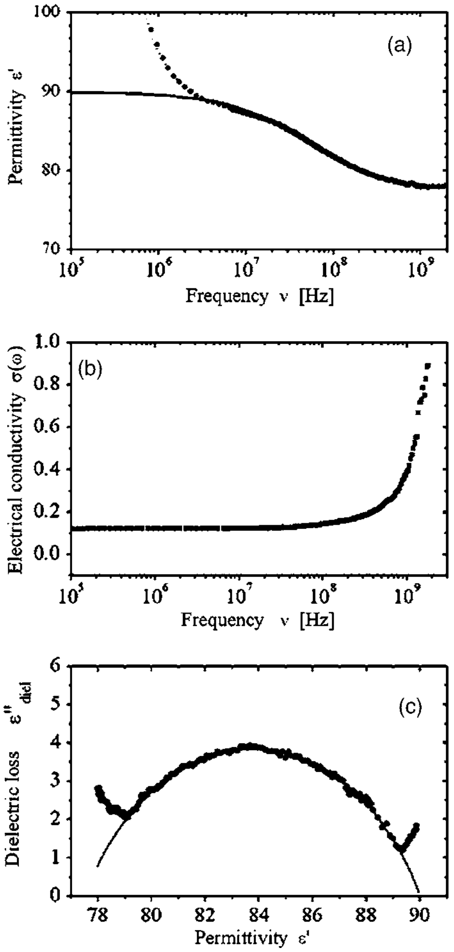

FIG. 3. A typical dielectric and conductometric spectra of 55%PMVP-Cl polyions in water (poor solvent) at the concentration of 10 mg/ml. (a) The permittivity $\epsilon'(\omega)$ as a function of the frequency. In the low-frequency tail of the spectrum, the data have been corrected by means of a CPA element [see Eq. (37)] to take into account the electrode polarization effect. The full line is the calculated values according to the real part of the Cole-Cole relaxation function [Eq. (36)] with the following values of the dielectric parameters: $\Delta\epsilon=12.5\pm0.1$, $\nu_{\rm ion}=46\pm2$ MHz, $\beta=0.26\pm0.02$. The high-frequency limit of the permittivity is $\epsilon_\infty=77.5\pm0.3$ and the low-frequency electrical conductivity is $\sigma_0=0.121$ mho/m. (b) The electrical conductivity $\sigma(\omega)$ as a function of the frequency. In the high-frequency tail, the orientational polarization of the aqueous phase is well-evidenced. (c) The Cole-Cole plot showing the "intermediate" relaxation together with the high-frequency tail of the electrode polarization effect (on the right) and the orientational polarization of the aqueous phase (on the left). The full curve is the calculated values on the basis of the fitting procedure employed. The values of the parameters are listed above.

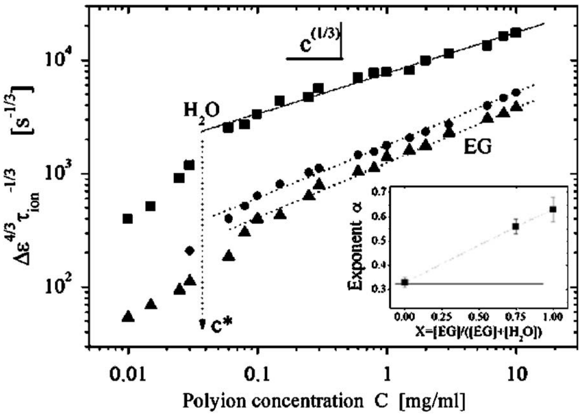

FIG. 4. Behavior of 55%PMVP-Cl in different ethylene glycol-water mixtures in the semidilute regime: (■): $X=0$ (pure water); (●): $X=0.75$; (▲): $X=1$ (pure ethylene glycol). The data have been analyzed according to the scaling relationship $\Delta\epsilon^{4/3}\tau_{\text{ion}}^{-1/3}\sim c^{\alpha}$. In poor solvent condition, $\alpha=1/3$ applies. The inset shows the exponent α for different solvent composition, from $X=0$, pure water, to $X=1$, pure ethylene glycol. The error bars indicate the uncertainties from the linear regression analysis. The expected value $\alpha=1/3$ is reached for 55%PMVP-Cl in water (poor solvent). The arrow mark the overlap concentration c^* for polymer in water.

polymer in ethylene glycol. These values agree remarkably well with the ones estimated from dielectric measurements in the case of 55%PMVP-Cl polyions. The agreement becomes a little worse in the case of 17%PMVP-Cl polyions because of the relatively small dielectric increment observed, particularly in the low-concentration region.

As can be seen in Figs. 4 and 5, water and ethylene glycol behave as poor and good solvent, respectively, for the partially charged PMVP-Cl polymer and the scaling laws predicted [Eqs. (33) and (34)] are valid. In particular, when the data are analyzed according to the relationship (34), valid for poor solvent condition, the expected value of the exponent in the polyion concentration dependence ($\alpha=1/3$) is attained for $X=0$ (pure water) while a progressive deviation is seen as the quality of the solvent changes, approaching that of good solvent, i.e., as the mole fraction of ethylene glycol is progressively increased. The same occurs when the same data are analyzed according to the relationship (33), valid for good solvent condition. In this case, as can be seen in Fig. 5, the expected value of the exponent in the polymer concentration dependence ($\alpha=1$) is observed at $X=1$ (pure ethylene glycol), whereas deviations are evidenced when the water concentration in the solution increases, i.e., when the solvent quality approaches the poor solvent condition. The inset in each of the two above stated figures clearly indicate how the scaling exponent deviates from the expected value ($\alpha=1/3$, $\alpha=1$, poor and good solvents, respectively) when the quality of the solvent is progressively changed.

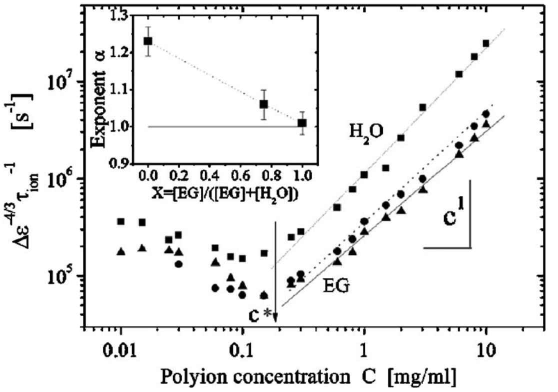

FIG. 5. Behavior of 55%PMVP-Cl in different ethylene glycol-water mixtures in the semidilute regime: (■): $X=0$ (pure water); (●): $X=0.75$; (▲): $X=1$ (pure ethylene glycol). The data have been analyzed according to the scaling relationship $\Delta\epsilon^{-4/3}\tau_{\text{ion}}^{-1}\sim c^{\alpha}$. In good solvent conditions, $\alpha=1$ applies. The inset shows the exponent α for different solvent composition, from $X=0$, pure water, to $X=1$, pure ethylene glycol. The error bars indicate the uncertainties derived from the linear regression analysis. The expected value $\alpha=1$ is reached for 55%PMVP-Cl in ethylene glycol (good solvent). The arrow marks the overlap concentration c^* for polymer in ethylene glycol.

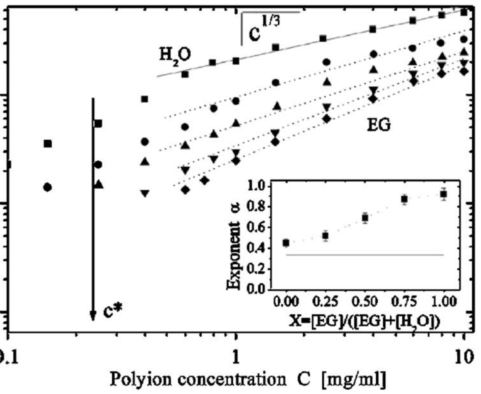

FIG. 6. Behavior of 17%PMVP-Cl in different ethylene glycol-water mixtures in the semidilute regime: (■): $X=0$ (pure water); (●): $X=0.25$; (▲): $X=0.5$; (▼): $X=0.75$; (♦): $X=1$ (pure ethylene glycol). The data have been analyzed according to the scaling relationship $\Delta\epsilon^{4/3}\tau_{\text{ion}}^{-1/3}\sim c^{\alpha}$. In poor solvent conditions, $\alpha=1/3$ applies. The inset shows the exponent α for different solvent composition, from $X=0$, pure water, to $X=1$, pure ethylene glycol. The expected value $\alpha=1/3$ is reached for 17%PMVP-Cl in water (poor solvent). The arrows mark the overlap concentration c^* for polymers in ethylene glycol.

In the case of polymer with degree of quaternization $Q=0.17$, the charge density parameter ξ is always less than unity for all the mixed solvents investigated and, in these conditions, counterion condensation within the Manning theory, should not occur. The polyions are expected to be fully ionized and counterions are free to fluctuate along the characteristic lengths of the chain.

Analogously to the previous case, the dielectric behavior of 17%PMVP-CL as a function of the polymer concentration C is shown in Figs. 6 and 7. In this case, the overlap concentration is about $c^*=0.17$ mg/ml for polymer in water and about $c^*=0.22$ mg/ml for polymer in ethylene glycol. These values are in agreement, to a first approximation, with the ones evaluated from dielectric measurements (marked by the arrows in Fig. 6) and, also in this case, the linear dependence expected from the scaling relationships (33) and (34) is

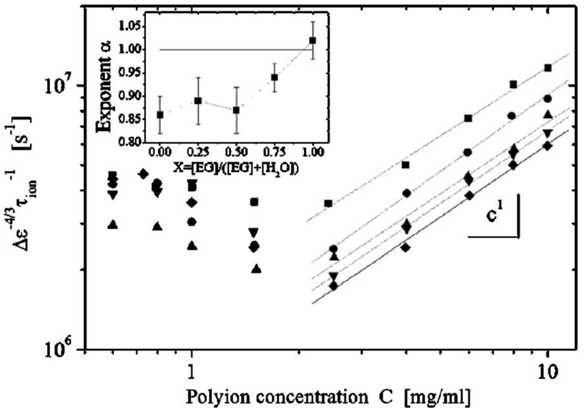

FIG. 7. Behavior of 17%PMVP-Cl in different ethylene glycol-water mixtures in the semidilute regime: (■): $X=0$ (pure water); (●): $X=0.25$; (▲): $X=0.5$; (▼): $X=0.75$; (◆): $X=1$ (pure ethylene glycol). The data have been analyzed according to the scaling relationship $\Delta\epsilon^{-4/3}\tau_{\text{ion}}^{-1}\sim c^{\alpha}$. In good solvent conditions, $\alpha=1$ applies. The inset shows the exponent α for different solvent composition, from $X=0$, pure water, to $X=1$, pure ethylene glycol. The expected value $\alpha=1$ is reached for 17%PMVP-Cl in ethylene glycol (good solvent).

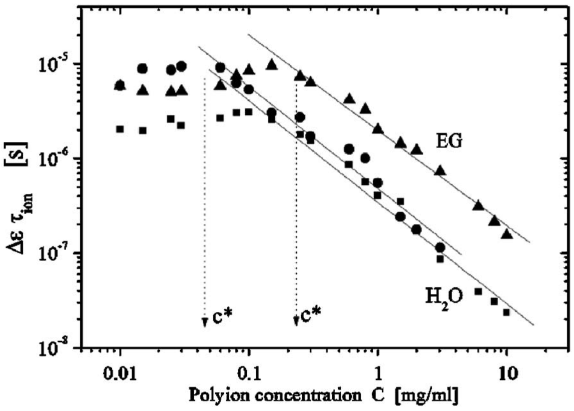

FIG. 8. Behavior of 55%PMVP-Cl in different ethylene glycol-water mixtures in the semidilute regime: (■): $X=0$ (pure water); (●): $X=0.75$; (▲): $X=1$ (pure ethylene glycol). The data have been analyzed according to the pearl necklace model [Eq. (35)], according to which the correlation length is given by Eq. (15) as the lines have slope -1 in water. The arrows mark the overlap concentration c^* for polymer in water and polymer in ethylebe glycol, respectively.

obeyed in the semidilute regime. The observed phenomenology is essentially the same and the appropriate scaling laws hold in poor and good solvent conditions, deviations being progressively put in evidence according to the change in the solvent quality. These results clearly show that the solvent quality has a definite influence on the polymer conformation since the only difference between the polymer investigated remains the quality of the solvent, changing progressively from good to poor.

When a polyelectrolyte chain is predicted to form a necklace structure in poor solvent and in semidilute regime, the correlation length along which counterions are assumed to fluctuate is given by Eq. (15) and the dielectric parameters should scale according to Eq. (35). In particular, $\Delta\epsilon$ is approximately constant and the relaxation time τ_{ion} scales as c^{-1}. As can be seen in Fig. 8, the data reasonably agree with this picture, over the whole semidilute regime. The dependence of $\Delta\epsilon\tau_{\text{ion}}$ on the inverse of concentration c implies that, at least in the semidilute regime, the product τf^{-1} should remain constant, to a first approximation, with the polyion concentration c. It should be noted that some results we have recently obtained [12] on the electrical conductivity properties of these polymers in the same solvents (water, ethylene glycol, and their mixtures) have evidenced, maintaining constant the solvent quality factor τ, a slight dependence of f on c. It would not be totally strange if dielectric and conductometric properties probed, in some way, "different" free counterions in the sense that counterions affecting the dielectric properties should lie in the vicinity of the polyion chain, whereas counterions that contribute to the electrical conductivity may reside relatively far from the chain and consequently their dependence on the concentration c may be a little different, depending on the chain conformation. The influence of condensed counterions has been recently considered by Chang and Yethiraj [23], who found that the chain collapse is accompanied by a migration of counterions to the vicinity of the polymer and that their concentration increases markedly once the chain has collapsed. Moreover, these authors found that the number of these "condensed" counterions is slightly dependent on the solvent quality, at least for sufficiently poor solvents (τ=0.5–1). This might justify that, within the experimetal uncertainties, $\Delta\epsilon\tau_{\text{ion}}$ scales as c^{-1}.

A comment on the dielectric behavior of the uncharged polymer P2VP is in order. In this case, there are no counterions in the solution deriving from the polymer ionization, as it happens in the case of the charged polymers, and the dielectric relaxation in the frequency range we have investigated is negligibly small and, in most cases, within the accuracy of our experimental setup. We observed a dielectric increment that hardly reaches a fraction of a dielectric unit only at the highest polymer concentration (about 10 mg/ml). This result confirms that the observed dielectric relaxation must be attributed to the counterion polarization originating from counterion fluctuation along some typical lengths, according to the model by Ito *et al.* [27].

V. CONCLUSIONS

The dielectric properties associated to the intermediate frequency relaxation process in polyelectrolyte solutions have been analyzed following the scaling theory developed by Dobrynin *et al.* [4] and Dobrynin and Rubinstein [11] on the basis of the electrostatic blob picture. Different scaling laws, according to the quality of the solvent, have been explicitly derived for the semidilute regime. In the case of poor solvent, when the chain adopts a pearl-necklace conformation, the scaling law predicts a linear dependence on the inverse of concentration c. We have compared these scaling predictions to the experimental results derived from the dielectric relaxation of two different charged polyions in mixed solvents, as the quality of the solvent is progressively varied from good solvent (ethylene glycol) to poor solvent (water) conditions. The solvent quality has a strong effect on the solution properties, as viewed from the dielectric point of view. This is clearly evidenced by the observed dependencies of the dielectric parameters (an appropriate combination of the dielectric increment $\Delta\epsilon$ and the relaxation time τ_{ion}) on the polyion concentration c, resulting in an exponent that is unity for good solvent and is $1/3$ for poor solvent condition, respectively. Moreover, in very poor solvents, when each chain forms a pearl-necklace structure, we find a very good agreement with the regime predicted by Dobrynin and Rubinstein [11] and called "string-controlled regime." In conclusion, these data provide reliable evidence for the scaling behavior of the dielectric properties of polyelectrolytes in solvents of different quality and give further support to the existence of a necklace-type conformation of the polymer chain under poor solvent condition.

ACKNOWLEDGMENT

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APPENDIX

In the framework of the Ito *et al.* model [27], the diffusion of counterions over a characteristic length l_0 (whatsoever its physical meaning) results in the scaling of the relaxation time τ_{ion} and of the dielectric increment $\Delta\epsilon$ according to the relationships

$$\tau_{\text{ion}} \sim l_0^2, \tag{A1}$$

$$\Delta\epsilon \sim fcl_0^2. \tag{A2}$$

Combining Eqs. (A1) and (A2) yields the scaling law

$$\frac{\Delta\epsilon}{\tau_{\text{ion}}} \sim fc. \tag{A3}$$

It is worth noting that, although the characteristic length l_0 depends on the concentration c, Eq. (A3) applies either in the dilute or in the semidilute regime. The "intermediate" frequency relaxation, independently of the quality of the solvent and of the concentration regime, obeys the scaling law given by Eq. (A3). In other words, this peculiar dependence can be assumed as an index in order to attribute, at a molecular level, the observed relaxation to counterion fluctuation. In the present case, for all the samples investigated, Fig. 9 clearly shows that $\Delta\epsilon/\tau_{\text{ion}}$ varies linearly with c, with a slope very close to unity. These findings give strong support to a description of an intermediate dielectric relaxation as originated from counterion fluctuation over a characteristic distance. Also this scheme supports the hypothesis that the fraction f of counterions should maintain constant over the whole concentration range investigated. In any case, these indications need further investigations to be more clearly ascertained.

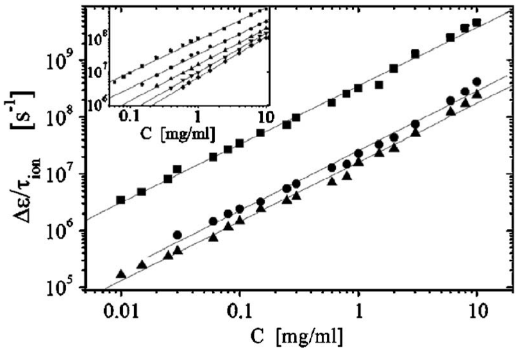

FIG. 9. The scaling behavior of 55%PMVP-Cl as the function of the polymer concentration C, according to the Ito *et al.* model (Ref. [27]). Three different solvent compositions have been investigated: (■): $X=0$ (pure water); (●): $X=0.75$; (▲): $X=1$ (pure ethylene glycol). The inset shows the behavior of 17%PMVP-Cl as a function of the polyion concentration C, for different composition of the solvent: (■): $X=0$ (pure water); (●): $X=0.25$; (▲): $X=0.5$; (▼): $X=0.75$; (◆): $X=1$ (pure ethylene glycol).

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