

Counterion condensation of differently flexible polyelectrolytes in aqueous solutions in the dilute and semidilute regime

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The low-frequency limit of the electrical conductivity (dc conductivity) of differently flexible polyions in aqueous solutions has been measured over an extended polyion concentration range, covering both the dilute and semidilute (entangled and unentangled) regime, up to the concentrated regime. The data have been analyzed taking into account the different flexibility of the polymer chains according to the scaling theory of polyion solutions, in the case of flexible polyions, and according to the Manning model, in the case of rigid polyions. In both cases, the fraction f of free counterions, released into the aqueous phase from the ionizable polyion groups, has been evaluated and its dependence on the polyion concentration determined. Our results show that the counterion condensation follows at least three different regimes in dependence on the polyion concentration. The fraction f of free counterions remains constant only in the semidilute regime (a region that we have named the Manning regime), while there is a marked dependence on the polyion concentration both in the dilute and in the concentrated regime. These results are briefly discussed in the light of the scaling theory of polyelectrolyte aqueous solutions.

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I. INTRODUCTION

Polyelectrolytes are macromolecules that, in appropriate solvents and, particularly, in aqueous solvents, dissociate into a polyion and low-mass ions (counterions) [1–3]. In spite of their ubiquitous presence in technological and biological processes, the complex phenomenology they present is still far to be completely understood and still eludes a complete description from a theoretical point of view. The dynamical properties of these systems, as manifested in electrophoretic mobility, diffusion, viscosimetry and transport processes under the influence of external driving forces, are deeply different from those of neutral polymers. Their peculiar behavior is mainly due to the coupling between electrostatic interactions among various charged units along the polyion chain, that gives rise to a very complex phenomenology.

As far as the transport properties are concerned, the peculiar feature which governs most of the polyelectrolyte behavior is the counterion condensation effect. When the linear charge density along the polyelectrolyte chain is sufficiently high, because of a fine balance between electrostatic attraction to the polyelectrolyte backbone and the loss in the conformational entropy when counterions are released in the bulk of the solution, a fraction of counterions remains localized in the immediate vicinity of the polyelectrolyte chain. Because of this “counterion condensation,” the effective charge of a polyelectrolyte chain differs from the one based on a stoichiometric ionization of its charged groups. As pointed out by Jeon and Dobrynin [4], the situation is even more complicated in the case of flexible, or partially flexible polyions, where the conformation of the chain, besides the concentration regime, depends on the quality of the solvent. For flexible polyelectrolytes, while for θ or good solvents for

the polyion backbone, counterion condensation results in a decrease of the polyion size with the increase of concentration, in a poor solvent condition, where the chain is modeled by a necklace of beads connected by strings of monomers, condensation occurs in an avalanchelike fashion [5–7].

A complete approach to these systems within the theory of polymer solution is rather difficult because of the intrinsic asymmetry of a polyelectrolyte solution, where we can roughly identify a polymer domain, where a highly charged flexible or partially flexible polyelectrolyte chain keeps a fraction of counterions, and a counterion domain formed by small ions (from the dissociation of the ionizable groups) and possibly by small cations and anions (carrying one or few charges) from the dissociation of added simple salt. Moreover, while in the polymer domain the charges are partially correlated along the polyion backbone, in the counterion domain charges can freely or almost freely diffuse.

Most of the structural and dynamical properties of polyelectrolytes, mainly in a biological context, are controlled by the charge density along the polyion chain as well as by the ionic strength of the surrounding aqueous phase. The knowledge of the transport parameters associated with the ion distribution inside the solution, both those bound to the immediate vicinity of the polyion and the more free ones in the bulk solution, is therefore particularly relevant in describing the behavior of the polyion chain in solution.

It is understandable then how electrical conductivity, that measures the contribution of every charged entity under the influence of an external electric field, represents a valuable probe to investigate the polyelectrolyte behavior in different environmental conditions [8].

We present here a set of low-frequency electrical conductivity (dc conductivity) measurements of polyelectrolytes of different chemical structures, different flexibility and different molecular weights in aqueous solutions (in the absence of added salt), over an extended concentration range, covering

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both the dilute and the semidilute regime. The results are presented and discussed in the light of the scaling theory of polyelectrolyte solutions.

We have chosen polyelectrolytes with main chains of different flexibility, such as the carboxymethylcellulose sodium salt with two different molecular weights, characterized by a rather rigid backbone, and such as the polyacrylate both in salty and acidic form and polystyrene sulfonic acid, whose backbones are largely flexible, although at a different extent.

The paper is organized as follows. In Sec. II, we review the basic equations dealing with the electrical conductivity of a polyelectrolyte solution and summarize the main predictions of the scaling theories of a polyelectrolyte solution according to the models proposed by Dobrynin *et al.* [9] for different concentration regimes. In Sec. III, we hint to the chemical characterization of the polyelectrolytes investigated and in Sec. IV we present some experimental results for the low-frequency electrical conductivity of the four different polyelectrolytes investigated in an extended concentration range. In particular, we present the behavior of the effective charge of the polyion chain or, equivalently, the fraction f of free counterions, in the different polymer concentration regimes. Finally, Sec. IV concludes with a brief discussion.

II. THEORETICAL BACKGROUND

An ensemble of charged particles at a numerical concentration n_i , each of them bearing an electric charge $z_i e$ and moving under the influence of an external electric field with a mobility u_i , is characterized by an overall electrical conductivity σ given by

$$\sigma = \sum_i (|z_i| e) n_i u_i. \quad (1)$$

In the case of a polyelectrolyte solution, in the absence of added salt, because of the partial ionization of the polymer charged groups (and the consequent counterion condensation effect), the macromolecules (at a concentration n_p , with a mobility u_p) and the released counterions (at a concentration n_1 and charge $z_1 e$) will contribute to Eq. (1), according to the relationship

$$\sigma = Z_{\text{pol}} e n_p u_p + z_1 e n_1 u_1, \quad (2)$$

where Z_{pol} and z_1 are the valencies of the polymer chain and of the counterions, respectively.

Consider a polyelectrolyte with degree of polymerization N , distance between charged groups b and fraction of charged monomers f . The Manning model [10,11] predicts a renormalization of the effective charge of the polyelectrolyte chain to a constant value above a condensation threshold. According to this theory, for a very long (infinite) linear polyelectrolyte and in the limit of infinite dilution, a complete release of the counterions towards the bulk solution occurs only when the average distance b between charges along the chain is larger than the Bjerrum length $l_B = e^2 / \epsilon K_B T$ (with e the elementary charge and ϵ the solvent permittivity). When b is smaller than l_B , electrostatic interactions increase and a fraction of counterions remains bound in the neighboring of the polyelectrolyte chain (counterion

condensation). In other words, according to the Manning theory, counterions condense until $l_B / b_{\text{eff}} = 1$, where e / b_{eff} is the effective linear charge density. Consequently, the fraction $(1-f)$ of counterions bound to the polyion chain, in order to reduce its effective charge to the critical value, will be given by $1 - b / l_B$.

Because of the counterion condensation effect, the charge of each chain is $Q_p = Z_{\text{pol}} e = f N z_p e$ and each chain will release into the aqueous phase $N f \nu_1$ counterions (each of them of charge $Q_1 = z_1 e$). Electroneutrality of the whole solution requires $z_p = \nu_1 z_1$ and Eq. (2) reads as

$$\sigma = N f e n_p (z_p u_p + z_1 \nu_1 u_1). \quad (3)$$

The mobility u_1 of counterions present in the solution is given by Manning [10,12], according to

$$u_1 = u_1^0 \frac{D_1}{D_1^0} - u_p \left(1 - \frac{D_1}{D_1^0} \right), \quad (4)$$

where u_1^0 is the limiting mobility in the pure aqueous phase and D_1 / D_1^0 is the ratio of the self-diffusion coefficient D_1 of counterions in the polyion solution and its value D_1^0 in the pure solvent. Substitution of Eq. (4) into Eq. (3) results

$$\sigma = N f e n_p z_1 \nu_1 \frac{D_1}{D_1^0} (u_1^0 + u_p). \quad (5)$$

This equation, written in the usual notations, by introducing the polyion concentration C_p in mol/l and the equivalent conductance of the polyion chain $\lambda_p = u_p F$, with F the Faraday constant, results as

$$\sigma = N f C_p \nu_1 z_1 \frac{D_1}{D_1^0} (\lambda_1^0 + \lambda_p). \quad (6)$$

The equivalent conductance λ_p , taking into account the asymmetry field effect [13,14], can be written as

$$\lambda_p = \frac{F Q_p \frac{D_1}{D_1^0}}{f_E + \frac{Q_p}{u_1^0} \left(1 - \frac{D_1}{D_1^0} \right)}, \quad (7)$$

where f_E is the usual electrophoretic coefficient (without the asymmetry field correction). This expression holds both when counterion condensation occurs and when it does not, the two cases being differentiated by the value of the polyion charge Q_p .

Finally, the electrophoretic coefficient f_E for a chain of N_0 simple spherical structural units of radius R_0 , following the general expression given by Kirkwood [14] can be written as

$$f_E = \frac{N_0 \zeta_{R_0}}{1 + \frac{\zeta_{R_0}}{6 \pi \eta N_0} \sum_i \sum_{i \neq j} \langle r_{ij}^{-1} \rangle} = \frac{N_0 \zeta_{R_0}}{1 + \frac{\zeta_{R_0}}{3 \pi \eta R_0} |\ln(k_D R_0)|}, \quad (8)$$

where $\zeta_{R_0} = 3 \pi \eta R_0$ is the friction coefficient, η is the viscosity of the aqueous phase, r_{ij} is the distance between different structural units, and $k_D = \sqrt{4 \pi l_b f c z_1^2}$ is the inverse of the Debye screening length. The sum in Eq. (8) has been evaluated

by introducing an appropriate cutoff function $\exp(-k_D r_{ij})$ and assuming a full extended chain with $r_{ij} = |i-j|R_0$ for $r_{ij} < 1/k_D$ [15].

The electrophoretic coefficient f_E depends on the particular conformation assumed by the polyion chain in the considered concentration regime, through the parameters N_0 and R_0 , and this quantity must be evaluated differently in the light of the different flexibility of the polyion chain and of the scaling model of polyion solutions.

A. Flexible polyions: The scaling approach

If we confine ourselves to flexible polyions in good solvent conditions and in dilute solution, the polyion chain is modeled as an extended rodlike configuration of $N_D = N/g_e$ electrostatic blob of size D , each blob containing g_e monomers and bearing an electric charge $q_D = z_p e f g_e$. 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 correlation blob containing g monomers and bearing an electric charge $q_{\xi_0} = z_p e f g$. Following the procedure adopted by Manning [16], in dilute regime, the elementary unit is the electrostatic blob and Eq. (8) becomes

$$f_E = \frac{N_D \zeta_D}{1 + \frac{\zeta_D}{3\pi\eta D} |\ln(1/N_D)|} \simeq \frac{3\pi\eta N_D D}{\ln(N_D)}, \quad (9)$$

where the friction coefficient ζ_D is simply given by

$$\zeta_D = 3\pi\eta D. \quad (10)$$

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

$$f_E = \frac{N_{\xi_0} \zeta_{\xi_0}}{1 + \frac{8\sqrt{N_{\xi_0}} \zeta_{\xi_0}}{3\sqrt{6\pi^3} \eta \xi_0}}, \quad (11)$$

where the friction coefficient ζ_{ξ_0} of the single rodlike structure of size ξ_0 can be derived from Eq. (9) with the substitution of $N_D D$ with ξ_0 and N_D with $N_D/N_{\xi_0} = g/g_e$,

$$\zeta_{\xi_0} = \frac{3\pi\eta\xi_0}{\ln(g/g_e)}. \quad (12)$$

In the dilute regime, the polyion equivalent conductance λ_p [Eq. (7)] depends, through the expression for the electrophoretic coefficient f_E , on the length of the full extended blob chain $N_D D$ and on the number N_D of blobs in each chain. According to Dobrynin *et al.* [9], these quantities scale with the fraction f of free counterions as

$$N_D D \sim N b (l_B/b)^{2/7} f^{4/7}, \quad (13)$$

$$N_D \sim N (l_B/b)^{5/7} f^{10/7}. \quad (14)$$

In the semidilute regime, the equivalent conductance λ_p [Eq. (7)], again through the expression for the electrophoretic coefficient f_E , depends on the contour length $N_{\xi_0} \xi_0$ of the ran-

dom walk chain of correlation blobs, on the number N_{ξ_0} of correlation blobs within each polymer chain and on the ratio g/g_e of the monomers inside a correlation blob to those inside an electrostatic blob. Again, according to Dobrynin *et al.* [9], these quantities scale as

$$N_{\xi_0} \xi_0 \sim N b (l_B/b)^{2/7} f^{4/7}, \quad (15)$$

$$N_{\xi_0} \sim N b^{3/2} c^{1/2} (l_B/b)^{3/7} f^{6/7}, \quad (16)$$

$$g/g_e \sim b^{-3/2} c^{-1/2} (l_B/b)^{2/7} f^{4/7}. \quad (17)$$

B. Rigid polyions

In the case of less flexible polyions, where the chain cannot be modeled as a sequence of electrostatic or correlation blobs, the electrophoretic coefficient f_E [Eq. (8)], and hence the electrical conductivity, depends on the number N_0 of structural units along the chain and on their size R_0 . In the dilute regime, these two quantities can be identified with the degree of polymerization N and with the mean distance between charged groups b , respectively. In the semidilute regime, the Kuhn formalism [17] can be applied and the conformation of the polymer chain can be described in terms of a statistical chain of N_k segments, each of them of length l_k . These parameters can be estimated through the total persistence length L_p and the end-to-end distance R_{ee} by means of the relationships

$$l_k = 2L_p \quad (18)$$

and

$$R_{ee} = \sqrt{\langle [R(L) - R(0)]^2 \rangle} = (N_k)^{1/2} l_k. \quad (19)$$

In this regime, the electrophoretic coefficient can be evaluated as a function of number of Kuhn segments as

$$f_E \simeq \frac{3\pi\eta N_k l_k}{\ln(N_k)}. \quad (20)$$

A summary of the different quantities involved in the conductivity behavior of the polyelectrolyte solutions, depending on the flexibility of the chain and on the concentration regime is given in Table I. These quantities have been employed in the electrical conductivity analysis.

C. Different concentration regimes

The behavior of polyelectrolyte aqueous solutions is characterized by different concentration regimes governed by four different zero-shear viscosity scaling laws [9,18]. We can identify three typical transition concentration thresholds, the concentration c^* , above which chains begin to overlap, the concentration c_e , at which entanglement effects begin and, finally, the concentration c_D , at which single electrostatic units (blobs or single monomers) start to overlap. For $c < c^*$ (dilute regime), each chain does not interact with others and an extended chain conformation is expected and the Zimm dynamics reasonably describes diffusive processes of

TABLE I. Number and kind of electrostatic units employed in the conductivity analysis. b is the mean distance between charges, l_k is the Kuhn length, ξ_0 is the correlation length of the polyions.

Structure	Dilute regime	Semidilute regime
Flexible	N_D, D [Eqs. (7) and (9)]	N_{ξ_0}, ξ_0 [Eqs. (7) and (11)]
Rigid	N_b, b [Eqs. (7) and (8)]	N_{l_k}, l_k [Eqs. (7) and (8)]

isolated chains. For $c^* < c < c_e$ (nonentangled semidilute regime), excluded volume and hydrodynamics interactions are screened and entanglement effects are weak. In this concentration regime, the Rouse dynamics applies and typical Fuoss law for the specific viscosity is expected. For $c > c_e$ (entangled semidilute regime), entanglement effects dominates. Significant overlap of chains occurs and topologically constrained motion results in a reptation-tube diameter larger than the correlation length [9]. Finally, for $c > c_D$, a concentrated regime holds. These different concentration regimes are characterized by different viscosity behaviors. The expected power laws for zero-shear specific viscosity is given by $\eta_s = (\eta - \eta_0) / \eta_0 \sim c_p^\nu$, where η is the viscosity of polyion solution, η_0 is the viscosity of the solvent, and c_p is the polyion concentration. The expected exponents ν of the polyion concentration dependence are listed in Table II. The specific viscosity $\eta_s = (\eta - \eta_0) / \eta_0$ of the different aqueous polyelectrolyte solutions investigated has been measured in order to evidenciate the different concentration regimes, with the further aim of determining, as accurately as possible, the boundary concentrations between the different regimes. Figures 1–3 show the specific viscosity η_s as a function of the polyion concentration. The different scaling regimes, characterized by different scaling exponents, are well evidenced. For all the systems, the concentrations c^* , c_e , and c_D are easily identified. The polyion concentrations are expressed as moles of monomers per liter.

III. EXPERIMENT

A. Materials

Polyacrylate in salty form [Na-PAA] and in acidic form [H-PAA], were purchased from Sigma Chem. Co. as 25 wt. % solutions in water. Sodium salt of carboxymethylcellulose [Na-CMC] of two different molecular weights 90 and 700 kD and degree of substitution 0.77 and 0.75, respectively, Polystyrene sulfonic acid [H-PSS] (18 wt. % in water solution) and poly(4-styrenesulfonic acid-co-maleic acid) so-

TABLE II. Expected scaling exponents for zero-shear specific viscosity [9,18] of aqueous polyion solutions in the four typical concentration regimes.

Specific viscosity $\eta_s = (\eta - \eta_0) / \eta_0$	Scaling exponent ν
$c < c^*$	1
$c^* < c < c_e$	1/2
$c_e < c < c_D$	1.5/1.7
$c > c_D$	15/4

dium salt [Na-PSS-Mal] were purchased from Sigma-Aldrich. Co. The samples were used as received, without any further purification.

The polyelectrolytes differ by flexibility, molecular weight and linear charge density. The sodium salt of poly(acrylic acid) is a water soluble polyelectrolyte with a relatively simple chemical repeating unit such that can be considered as a model flexible polyion. Na-CMC molecules assume a rather extended, rodlike, conformation at low concentrations but, at higher concentrations, the molecules overlap and coil up until they behave as a thermoreversible gel. PSS is probably the most widely studied synthetic polyelectrolyte, with a rather flexible chain at room temperature. The main structural and chemical characteristics of the polymers investigated are listed in Table III.

All the solutions were prepared at the desired polymer concentration (in the range from 10^{-2} mg/ml to 100 mg/ml, in order to completely cover the dilute and semidilute concentration regime) with deionized Q-quality water (Millipore) whose dc electrical conductivity was less than $1-2 \mu\text{S/cm}$ at room temperature.

B. Electrical conductivity measurements

The electrical conductivity measurements were carried out by means of an Impedance Analyzer Hewlett-Packard

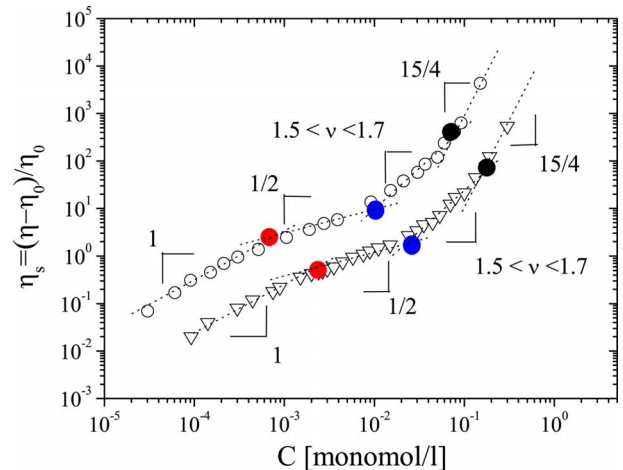


FIG. 1. (Color online) Specific viscosity η_s as a function of polyion concentration for Na-CMC-90 kD (∇) and Na-CMC-700 kD (\circ). The dotted lines represent the expected power-law behaviors according to the different concentration regimes as shown in Table II. The thick dots mark the boundary concentrations between dilute and semidilute unentangled (c^*), semidilute unentangled and semidilute entangled (c_e), semidilute entangled and concentrated (c_D) regimes, respectively.

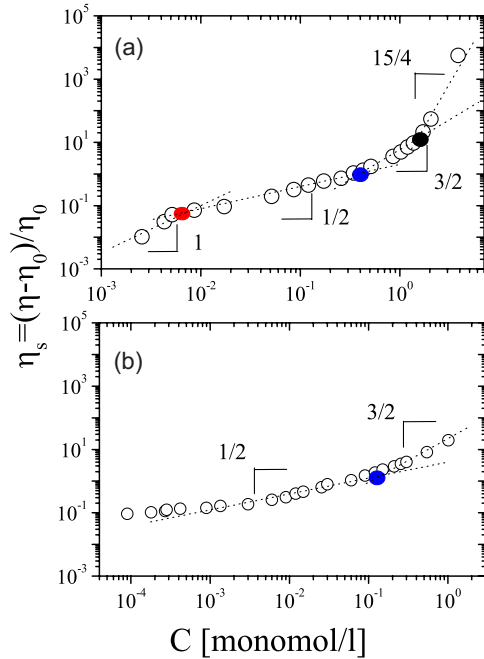


FIG. 2. (Color online) Specific viscosity η_s as a function of polyion concentration for NaPSS-Mal 20 kD [panel (a)] and H-PSS 75 kD [panel (b)]. The dotted lines represent the expected power-law behaviors according to the different concentration regimes as shown in Table II. The thick dots mark the boundary concentrations between dilute and semidilute unentangled (c^*), semidilute unentangled and semidilute entangled (c_e), semidilute entangled and concentrated (c_D) regimes, respectively.

model 4192A over the frequency range from 40 Hz to 110 MHz. All measurements have been carried out at the temperature of 25.0 °C within 0.1 °C. The conductivity cell consists in a short section of a cylindrical coaxial line (inner conductor 3 mm in diameter, electrode spacing 2 mm) connected to the meter by means of a precision APC7 connector. The cell constants have been determined by a calibration procedure with standard liquids of known conductivity and dielectric constant, according to a procedure reported elsewhere [19,20]. Here, we will deal exclusively with the low-frequency limit of the measured electrical conductivity, obtained by averaging the conductivity values at frequencies in the range between 10 and 100 kHz, where only the dc contributions are present, being completely negligible the contributions due to the dielectric loss (dc conductivity) and the electrode polarization effect, dominant at very low frequencies, is still negligible. The behavior of the electrical conductivity as a function of the frequency will be presented and discussed in a forthcoming paper [21].

C. Polyelectrolyte behavior

All the polymer chains have, on the average, at least one ionizable group per monomer with a mean distance b between charges (Table III). In aqueous solution, the charge density parameter l_b/b is larger than the critical value ($l_b/b = 1$) and according to the Manning-Oosawa theory [10], counterion condensation will occur. However, it is worth not-

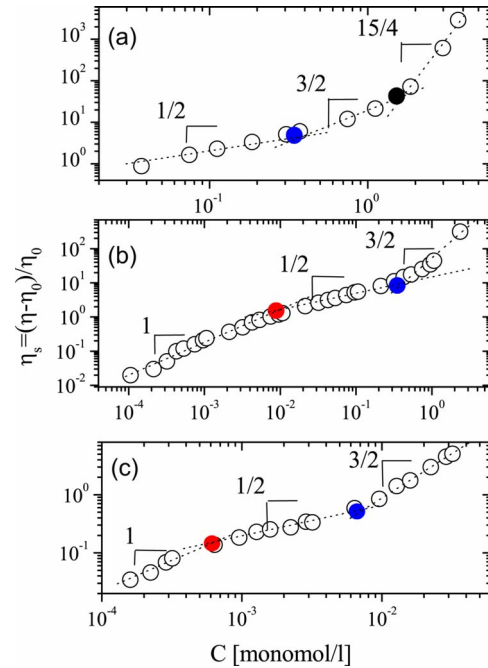


FIG. 3. (Color online) Specific viscosity η_s as a function of polyion concentration for Na-PAA 60 kD [panel (a)], Na-PAA 225 kD [panel (b)], 4000 kD [panel (c)]. The dotted lines represent the expected power-law behaviors according to the different concentration regimes as shown in Table II. The thick dots mark the boundary concentrations between dilute and semidilute unentangled (c^*), semidilute unentangled and semidilute entangled (c_e), semidilute entangled and concentrated (c_D) regimes, respectively.

ing that in extremely dilute polyelectrolyte solutions, because of the huge entropy gain occurring when single-chain system passes from a counterion-condensed state to a counterion-uncondensed state, deviation from the Manning condensation theory should be expected. Such deviations, suggested also by numerical simulations [22], have been observed in different polyelectrolyte systems [23–26].

IV. RESULTS AND DISCUSSION

The low-frequency electrical conductivity σ of the different polyion aqueous solutions investigated are shown in Figs. 4–6. Measurements extend over a wide range of polyion concentration, covering the dilute and semidilute regime, up to the beginning of concentrated regime. As can be seen, when plotted in a double log scale, the conductivity σ shows a marked power-law behavior, with marked deviations both at low and high concentrations. These deviations are more relevant in the case of the copolymer Na-PSS-Mal and of the polymer H-PAA. The electrical conductivity data have been analyzed on the basis of the above-stated theoretical framework, with the appropriate expressions for polyion equivalent conductivity, according to the concentration regime and the flexibility of the polyion chain.

For flexible polyelectrolytes, the elementary units are electrostatic blobs and correlation blobs at low (dilute regime) and high (semidilute regime) concentration, respectively. The appropriate expressions for the polyion conduc-

TABLE III. Molecular weight M_w , degree of polymerization N , number of persistence lengths Nb/L_p (values of L_p can be founded in Refs. [27–29]), distance between charged groups b and flexibility properties of the polyelectrolytes investigated.

	M_w [kD]	N	b [Å]	Nb/L_p	Structure
CMC (I)	90	400	6.68	≈ 17	Rigid
CMC (II)	700	3200	6.87	≈ 137	Rigid
Na-PAA	60	638	2.52	≈ 230	Flexible
Na-PAA	225	2392	2.52	≈ 861	Flexible
Na-PAA	4000	42530	2.52	≈ 15311	Flexible
H-PAA	60	638	2.52	≈ 230	Flexible
H-PSS	75	407	2.50	≈ 101	Flexible
Na-PSS-Mal	20	103	3.30	≈ 34	Flexible

tivity in dilute and semidilute regimes are given by Eqs. (6) and (7), where the electrophoretic coefficients are given by Eq. (9) for $c < c^*$ and by Eq. (11) for $c > c^*$. For rigid polyelectrolytes, we cannot consider the monomer chains as a linear sequence of blobs of size D or a sequence of correlation blobs of size ξ_0 and we will consider, as simple electrostatic units, the segments of length b and the Kuhn length l_k in dilute and semidilute regimes, respectively. In other words, for semidilute flexible polymer solutions, we will assume the chain composed by a sequence of Kuhn segments,

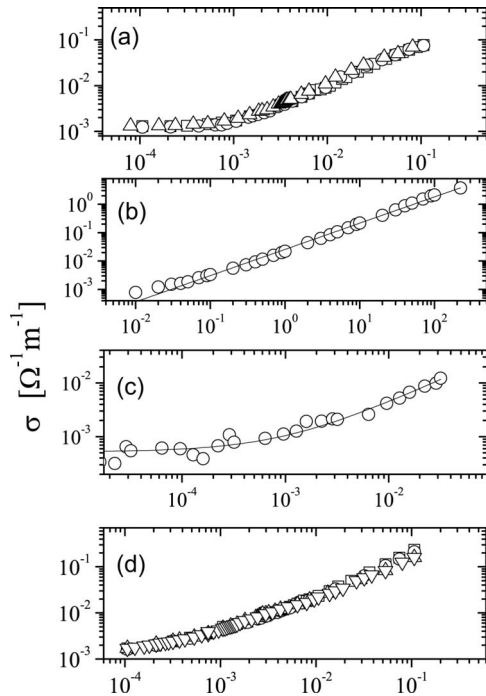


FIG. 4. The low-frequency electrical conductivity σ of polyacrylate 60, 225, and 4000 kD molecular weight in salty form [Na-PAA] [panels (a), (b), and (c), respectively] and in acidic form [H-PAA] [panel (d)] as a function of the polyion concentration, at the temperature of 25.0 °C. In panels (a) and (d), different symbols refer to three independent sets of measurements on independent sample preparations. The polyelectrolyte concentrations span different ranges, according to the different solubility. Full lines are guides for the eye only.

in which the Kuhn length plays the role of the correlation length ξ_0 in the case of more flexible polyions within the semidilute regime.

Equations (6) and (7) for the electrical conductivity and equivalent conductance in dilute and semidilute regime depend on a single free parameter, the fraction f of free counterions, the other parameters being known through the structural properties of the polyion backbone or assumed to be known within the theoretical framework employed. By means of a nonlinear least-squares-fitting procedure of the above-stated models to the experimental results, the values of f , over the whole concentration range investigated, can be obtained.

Figures 7–9 show this parameter as a function of polyelectrolyte concentration C for the different systems investigated. At a first look, for all the systems, there is a pronounced decrease of f as polymer concentration increases, this decrease extending approximately over the whole dilute regime. This finding is in agreement with previous theoretical and other experimental results [23–26,30,31].

For all the polyelectrolytes investigated and for semidilute (nonentangled) regime, $c^* < c < c_e$, a more or less extended

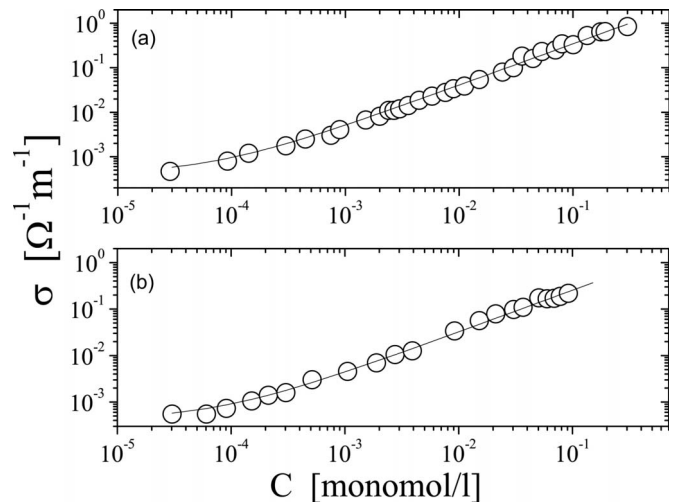


FIG. 5. The low-frequency electrical conductivity σ of Na-CMC as a function of the polyion concentration, at the temperature of 25.0 °C, at two different molecular weights: [panel (a)] 90 kD; [panel (b)] 700 kD. Full lines are guides for the eye only.

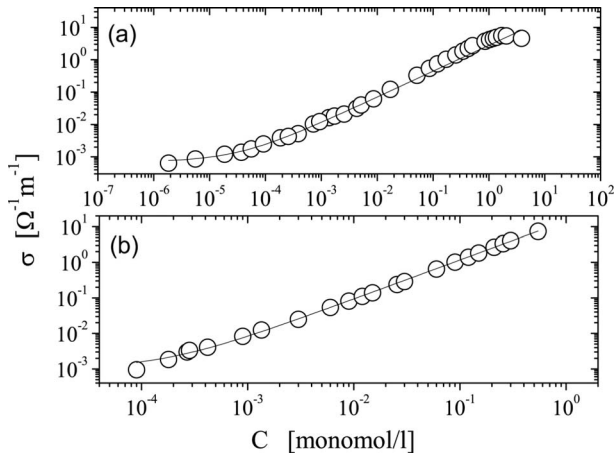


FIG. 6. [Panel (a)] The low-frequency electrical conductivity σ of Na-PSS-MAL 20 kD molecular weight as a function of the polymer concentration, at the temperature of 25.0 °C. [Panel (b)] The analogous quantity for H-PSS 75 kD molecular weight. Full lines are guides for the eye only.

plateau is reached and we will name this phase as the Manning regime [23,24]. This dependence is of course unexpected within the classical Manning model, that for a linear infinite rigid polyelectrolyte, in the limit of infinite dilution, predicts a fraction of free counterions fixed to the value f_{th} defined by the ratio between the nominal charge spacing b and Bjerrum length l_b [10] according to

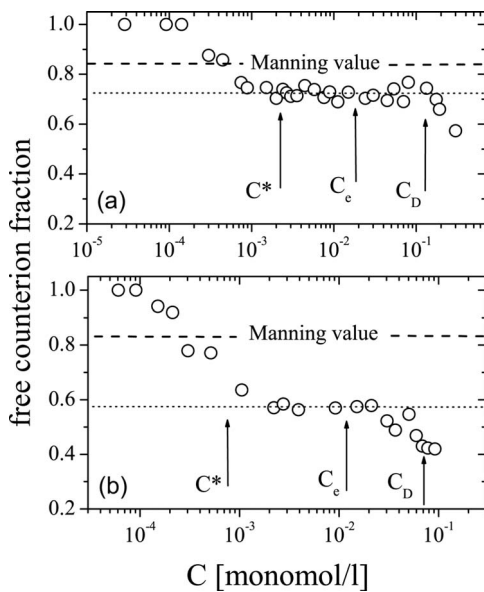


FIG. 7. The fraction f of free counterions in Na-CMC aqueous solutions as a function of the polymer concentration. [Panel (a)] Na-CMC 90 kD; [panel (b)] Na-CMC 700 kD. The arrows mark transition concentrations as deduced from the viscosity measurements. Dashed line indicates the f value predicted by Oosawa-Manning theory while the dotted line is the mean value $\langle f \rangle$ in the Manning regime.

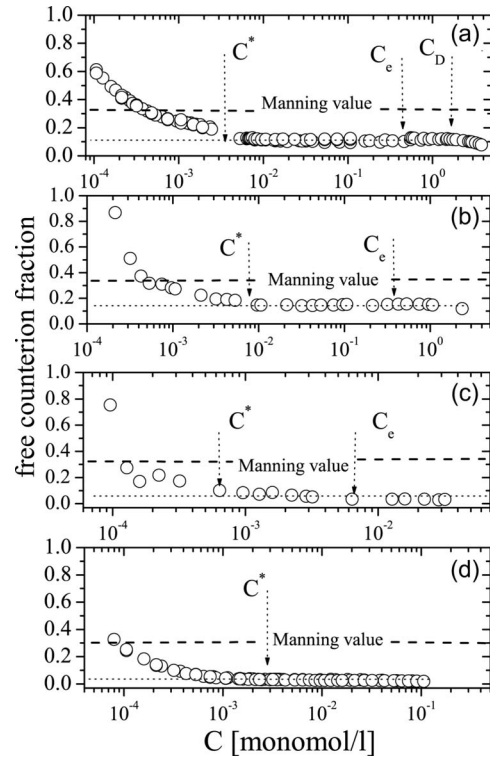


FIG. 8. The fraction f of free counterions in Na-PAA 60 kD [panel (a)], Na-PAA 225 kD [panel (b)], Na-PAA 4000 kD [panel (c)], and H-PAA 60 kD [panel (d)] aqueous solutions as a function of the polymer concentration. The arrows mark transition concentrations as deduced from the viscosity measurements. Dashed line indicates f value predicted by Oosawa-Manning theory while the dotted line is the mean value $\langle f \rangle$ in the Manning regime.

$$f_{th} = 0.886|z_1|^{-1}\xi^{-1}, \quad \xi = \frac{l_b}{b}, \quad (21)$$

where ξ is the charge density parameter. While a constant value is observed, its level is significantly lower than the one predicted by Manning [Eq. (21)].

As far as the CMC polyions are concerned, we observe that the level at which the fraction f of free counterions maintains constant, within the semidilute regime, is rather different for the two CMC samples. This difference could be due to a different degree of substitution leading to a different stoichiometric linear charge density. However an effect of the degree of polymerization on the value of f has been previously observed in different other works [23,32] in aqueous polystyrene sulfonate sodium salt [Na-PSS] and in various poly(vinyl-benzyl-trialkyl ammonium) chloride aqueous solutions. Moreover, a concentration dependence of the fraction f of free counterions has been measured in a variety of polyion solutions such as, for example, in sodium polyacrylate salt 225 kD molecular weight in the presence of added NaCl [33], again in sodium polyacrylate salt solution at high concentration [13,15] and in differently structured compounds of poly(vinyl-benzyl-trialkyl ammonium) chloride or in sodium poly(styrene sulfonate) [23,24]. With the increase of the degree of polymerization, the partial increase of the

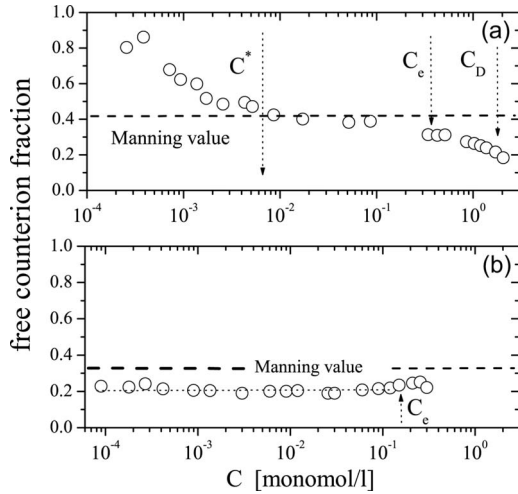


FIG. 9. The fraction f of free counterions in Na-PSS-Mal [panel (a)] 20 kD and H-PSS 75 kD [panel (b)] aqueous solutions as a function of the polymer concentration. The arrows mark transition concentrations as deduced from the viscosity measurements. Dashed line indicates f value predicted by Oosawa-Manning theory while the dotted line is the mean value $\langle f \rangle$ in the Manning regime.

chain flexibility and the partial overlap between polyelectrolyte chains influence the amount of the net charge Nf of the single chains and determine the characteristic value of the fraction f of free counterions within the Manning regime that, as shown in Figs. 7–9, has always a lower value than the theoretical prediction [Eq. (21)].

It is worth noting that the so-called Manning regime begins at the concentration c^* , which defines the boundary between dilute and semidilute regime. From viscosity measurements, these concentrations fall at $c^* = 0.38$ mg/ml and $c^* = 0.15$ mg/ml for CMC-90 kD and CMC-700 kD, respectively. These concentrations agree reasonably well with the ones calculated from the relationship $c^* = N/R_{ee}$, that yields values of about 0.3 and 0.1 mg/ml, respectively.

In the case of flexible polyelectrolytes, i.e., Na-PAA, H-PAA, Na-PSS-Mal, and H-PSS polyions, the conductivity data have been analyzed according to the scaling model of a polyelectrolyte solution and the resulting fraction f of free counterions is shown in Figs. 8 and 9. As can be seen, also in these cases, the same phenomenology appears, with a well-defined constant interval for the f values, corresponding, in all the cases investigated, to the semidilute regime. For all the samples investigated, at concentrations close to c_D , there is a decrease of f , this behavior being as evident as in the case of less flexible polyions.

For the sake of completeness, we remark that if we had extended the Manning model to flexible polyions (either considering a sequence of subunits of length b or a sequence of subunits of length l_k), an inconsistency would have been found, with values of f largely meaningless in extended concentration ranges. This fact supports the need to use a different theoretical framework (the scaling model of a polyion solution) in the case of flexible polyions.

A final comment is in order. In the case of rigid polyelectrolytes, we have differently analyzed the conductivity data. If the model adopted in the dilute regime had been extended

to the semidilute regime, considering the elementary unit as a segment of length b_{eff} and the number of segment given by Nb/b_{eff} , the results, as far as the fraction f of free counterions, would not have been sensibly different from the ones obtained (Fig. 7) considering a change in the length scale of basic electrostatic unit from the monomer length b to the Kuhn length l_k . This result furnishes further support to the analysis of conductivity data employing different models in consequence of different conformation of the polyion in solution.

V. CONCLUSIONS

In this paper, taking advantage of the scaling picture of a polyelectrolyte solution according to the theory developed by Dobrynin, Colby, and Rubinstein [9,34], we present, for a series of differently flexible polyelectrolytes, how the fraction f of free counterions, due to the counterion condensation, varies with the polyelectrolyte concentration. These results offer further support to the fact that the effective charge of a polyion chain, after counterion condensation has occurred, depends on the polymer concentration regime. In other words, the distribution of free counterions in the bulk solution is influenced by the presence of neighboring chains and, even more, by the conformation they assume in the different concentration regime.

Furthermore, we have observed the presence of a Manning regime, where the fraction f of free counterions remains practically constant, when it coincides with the unentangled semidilute regime. In this regime, the value of the free counterion fraction is lower than the one predicted by classical Manning theory at finite concentration [35]. On the other hand, for all the polyelectrolytes investigated, the dilute regime is characterized by monotonic decrease of free counterion fraction as polyelectrolyte concentration is increased in accordance with previous theoretical results [25,30] that strongly underly the importance of entropic effects at infinite dilution.

The influence of the different chain flexibility effects has been taken into account using the scaling blob model [9] to analyze flexible chains (Na-PAA, H-PAA, H-PSS, and Na-PSS-Mal polyions) and a simple Manning scheme for rigid polyions (CMC-90 kD and CMC-700 kD). At high concentration regime, for $c > c_e$ and for all polyions investigated, f shows a further decrease that is more pronounced in the proximity of the concentrated regime ($c > c_D$), where single electrostatic units start to overlap and where single counterion is somehow trapped between chains so that it cannot contribute to the specific conductivity of the solution. These counterions lead to a sharp decrease of free counterion fraction.

The above analysis is for the time being confined to polyions in good solvent condition, but it could be extended to polyions in poor solvent conditions, where a strong restructuring of the polyion chain within the necklace model [5] is expected. These investigations may give useful information on the conformation of a polyion in solution in different concentration regimes and offer further insight on the mechanism of the electrical conductivity of polyelectrolyte aqueous solutions.

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