The counterion condensation of differently flexible polyelectrolyte aqueous solutions in the dilute and semidilute regime

D. Truzzolillo, F. Bordi, C. Cametti and S. Sennato
Dipartimento di Fisica, Università di Roma “La Sapienza”, Piazzale A. Moro 5, I-00185 Rome (Italy) and CNR INFM-SOFT, Unità di Roma1.
(Dated: June 13, 2008)

The low-frequency limit of the electrical conductivity (d.c. conductivity) of differently flexible polyelectrolytes 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 polymers, and according to the Manning model, in the case of rigid polymers. 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 at the light of the aqueous ionic solutions.

PACS numbers: 82.35.Rs, 61.25.Hq, 36.20.-r

Keywords: Electrical conductivity, aqueous polion solutions, counterion condensation effect.

I. INTRODUCTION

Polyelectrolytes are macromolecules that, in appropriate solvents and, in most cases, in aqueous solvents, dissociate into a macroion and low-mass ions (counterions) \[1,2\]. In spite of their ubiquitous presence in technological and mostly 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 polyelectrolyte chain, that gives rise to a very complex phenomenology whose understanding is still rather poor.

As far as the transport properties are concerned, the peculiar feature which governs most of the polyion behavior is the counterion condensation effect, for which the effective charge of a polyion chain differs from the one based on a stoichiometric ionization of its charged groups. Based on 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 (counterion condensation). As pointed out by Jeon and Dobrynin \[3\], the situation is even more complicated in case of flexible, or partially flexible polyions, where the conformation of the chain, besides the concentration regime, depends on the quality of the solvent. 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 poor solvent condition, where the chain is modeled by a necklace of beads connected by strings of monomers, condensation occurs in an avalanche-like fashion \[4,5,6\].

A complete approach to these systems within the theory of polymer solution is rather difficult because of the intrinsical 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, in some cases, by 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 polyelectrolyte 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 polyelectrolyte 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 polyelectrolyte backbone, and the more free ones in the bulk solution, is therefore particularly relevant in describing the behavior of the polyelectrolyte 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 polyion behavior in different environmental conditions.

We present here a set of low-frequency electrical conductivity (d.c. conductivity) measurements of polyions of different chemical structures, different flexibility and different molecular weights in aqueous solutions (in absence of added salt), over an extended concentration range, covering 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 polyions with main chains of different flexibility, such as carboxymethylcellulose sodium salt of two different molecular weights, whose backbone is rather rigid, and such as polycrylate, in salty and acidic form, and polystyrene sulfonic acid, whose backbones are largely flexible, even if 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 polyion solution and summarize the main predictions of the scaling theories of a polyelectrolyte solution according to the models proposed by Dobrynin et al. [7] for different concentration regimes. In Sec. III, we hint to the chemical characterization of the polyions investigated and in Sec. IV we present some experimental results for the low-frequency electrical conductivity of the four different class of polyions 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 polyion 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 \( \sigma \) given by

\[
\sigma = \sum_i (|z_i| e) n_i u_i
\]

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

\[
\sigma = Z_{pol} e n_p u_p + z_1 e n_1 u_1
\]

where \( Z_{pol} \) and \( z_1 \) are the valencies of the polyion chain and a counterion, respectively.

Consider a polyion with degree of polymerization \( N \), size of the monomers \( b \) and fraction of charged monomers \( f \). The Manning model [8, 9] predicts a re-normalization of the effective charge of the polyion chain to a constant value above a condensation threshold. According to this theory, for a charged infinite linear polyion in very dilute condition, a complete ionizable groups dissociation occurs only when electrostatic repulsion is weaker than the thermal energy \( K_B T \); in other words, when the average distance \( b \) between charges along the chain is larger than the Bjerrum length \( l_B = e^2 / K_B T \) (with \( e \) the elementary charge and \( \epsilon \) the permittivity of the aqueous phase). When \( b \) is smaller than \( l_B \), electrostatic interactions increase and a fraction of counterions remains bound in the neighboring of the polyion chain (counterion condensation). In the Manning theory, counterions condense until \( b/eff = 1 \), where \( b/eff \) is the effective distance between dissociated groups. Consequently, the fraction \((1 - f)\) of counterions bound to the polyion chain, in order to reduce its effective charge to the critical value, will given by \( 1 - b/l_B \).

Because of the counterion condensation effect, the charge of each chain is \( Q_p = Z_{pol} e = f N z_p e \) and each chain will release into the aqueous phase \( N f z_1 \) 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

\[
\sigma = N f e n_p (z_p u_p + z_1 \nu_1 u_1)
\]

The mobility \( u_1 \) of counterions present in the solution is given by Manning [8, 10], according to

\[
u_1 = u_1^0 \frac{D_1}{D_1^0} - u_p (1 - \frac{D_1}{D_1^0})
\]

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

\[
\sigma = N f e n_p z_1 \nu_1 \frac{D_1}{D_1^0} (u_1^0 + u_p)
\]

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

\[
\sigma = N f C_p \nu_1 \frac{D_1}{D_1^0} (\lambda_1^0 + \lambda_p)
\]

The equivalent conductance \( \lambda_p \), taking into account the asymmetry field effect [11, 12], can be written as

\[
\lambda_p = \frac{F Q_p}{f E + Q_p \nu_1 (1 - \frac{D_1}{D_1^0})}
\]

where \( f E \) is the usual electrophoretic coefficient (without the asymmetry field correction). This expression holds both when counterion condensation occurs and when
does not, the two case being differentiated by the value of the polion 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 [12] can be written as

$$ f_E = \frac{N_0 \zeta R_0}{1 + \frac{\zeta R_0}{3 \pi \eta N_0} \sum_i \sum_{i \neq j} (r_{ij}^{-1})} = \frac{N_0 \zeta R_0}{1 + \frac{\zeta R_0}{3 \pi \eta N_0} |\ln(k_D R_0)|} $$

where $\zeta R_0 = 3 \pi \eta R_0$ is the friction coefficient, $\eta$ the viscosity of the aqueous phase and $r_{ij}$ the distance between different structural units and $k_D = \sqrt{4 \pi \eta_0 R c e^2}$ the inverse of the Debye screening length. The sum in eq. \[8\] has been evaluated by introducing an appropriate cut-off function $\exp(-k_D r_{ij})$ and a full extended polion chain with $r_{ij} = |i - j| R_0$ [13].

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, in dilute solution, the polion chain is modeled as an extended rod-like configuration of $N_D = N/g_e$ electrostatic blob of size $D$, each blob containing $g_e$ monomers and bearing an electric charge $q_D = z_p e g_f g_e$.

In the semidilute regime, the polyion chain is modeled as a random walk of $N_{\xi_0} = N/g$ correlation blobs of size $\xi_0$, each correlation blob containing $g$ monomers and bearing an electric charge $q_{\xi_0} = z_p e g_f g_e$. Following the procedure adopted by Manning [14], in dilute regime, the elementary unit is the electrostatic blob and eq. \[8\] becomes

$$ f_E = \frac{N_{DD} D}{1 + \frac{\zeta D}{3 \pi \eta D} |\ln(1/N_D)|} \sim \frac{3 \pi \eta N_{DD} D}{\ln(N_D)} $$

where the friction coefficient $\zeta_D$ is simply given by

$$ \zeta_D = 3 \pi \eta D $$

In the semidilute regime, where the single unit is the correlation blob of size $\xi_0$, the electrophoretic coefficient $f_E$ for a random walk of $N_{\xi_0}$ correlation blobs is given by

$$ f_E = \frac{N_{\xi_0} \zeta_{\xi_0}}{1 + \frac{8 \sqrt{N_{\xi_0} \zeta_{\xi_0}}}{3 \sqrt{6} \pi \eta \xi_0}} $$

where the friction coefficient $\zeta_{\xi_0}$ of the single rod-like structure of size $\xi_0$ can be derived from eq. \[9\] with the substitution of $N_{DD}$ with $\xi_0$ and $N_D$ with $N_D/N_{\xi_0} = g/g_e$,

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

1. The scaling laws in the scaling polyion model

In the dilute regime, the polion equivalent conductance $\lambda_p$ (eq. \[7\]) depends through the expression for the electrophoretic coefficient $f_E$ on the length of the full extended chain $N_{DD}$ and on the number $N_D$ of blobs in each chain. According to Dobrynin et al. [7], these quantities scale with the fraction $f$ of free counterions as

$$ N_{DD} \sim N b(l_B/b)^{2/7} f^{4/7} $$

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

In the semidilute regime, the equivalent conductance $\lambda_p$ (eq. \[7\]), again through the expression for the electrophoretic coefficient $f_E$, depends on the contour length $N_{\xi_0} \zeta_0$ of the random walk chain of correlation blobs, on the number $N_{\xi_0}$ 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. [7], these quantities scale as

$$ N_{\xi_0} \zeta_0 \sim Nb(l_B/b)^{2/7} f^{4/7} $$

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

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

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 degree of polymerization $N$ and with the monomer size $b$, respectively. In the semidilute regime, the Khun formalism [15] can be applied and the conformation of the polymer chain can be described in terms of a statistical chain of $N_{lb}$ segments, each of them of length $l_k$. These parameters can be estimated through the persistence length $L_p$ and the end-to-end distance $R_{EE}$ by means of the relationships

$$ l_k = 2L_p $$

and

$$ R_{EE} = \sqrt{\langle(R(L) - R(0))^2 \rangle} = (N_{lb})^{1/2} l_k $$

A summary of the different quantities involved in the conductivity behavior of the polyion solutions, depending on the flexibility of the chain and on the concentration regime is given in Tab. \[4\] These quantities have been employed in the electrical conductivity analysis.
and the polyion concentration dependence are given by \[ \eta_{\text{c}} \sim (\eta - \eta_0)/(\eta - \eta_0^0) \] where \( \eta \) is the viscosity of the solvent, \( \eta_0 \) is the viscosity of the polyion solution, \( \eta_0^0 \) and \( \eta^0 \) are the respective viscosities of the solvent and the polyion solution. The expected exponents \( \nu \) of the polyion concentration dependence are listed in Tab. III. The reduced viscosity \( \eta_s = (\eta - \eta_0)/(\eta - \eta_0^0) \) of the different aqueous polyion solutions investigated has been measured in order to evidence the different concentration regimes, with the further aim of determining, as accurately as possible, the boundary concentrations between the different regimes. Figs. 1 and 2 show the reduced viscosity \( \eta_s \) 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.

### III. EXPERIMENTAL

#### A. Materials

Polyacrylate in salty form [Na-PAA] and in acidic form [H-PAA], were purchased from Sigma-Aldrich Co. as 25 wt\% solutions in water. Sodium salt of carboxymethylcellulose [Na-CMC] of two different molecular weights (90 and 700 kD), Polystyrene sulfonic acid [H-PSS] (18 wt\% in water solution) and Poly(4-styrenesulfonic acid-maleic acid) sodium salt [Na-PSS-MA] were purchased from Sigma-Aldrich Co. The samples were used as received, without any further purification.

The polymers differ by flexibility, molecular weight, linear charge density. The sodium salt of poly(acrylic acid) is a water soluble polyelectrolyte with a relatively simple chemical repeat unit such that it can be considered as a model flexible polymer. Na-CMC molecules assume a rather extended, rod-like, conformation at low concentrations, 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 Tab. III. All the solutions were prepared at the desired polymer concentration (in the range from 10^{-2} mg/ml to

| Structure | Dilute regime | Semidilute regime |
|----------|--------------|------------------|
| Flexible | \( N_p, D \) (eqs. 7, 9) | \( N_0, \xi_0 \) (eqs. 10, 11) |
| Rigid | \( N_b, b \) (eqs. 7, 8) | \( N_k, l_k \) (eqs. 7, 8) |

**TABLE I:** Number and type of electrostatic units employed in the conductivity analysis. \( b \) is the mean distance between charges, \( l_k \) is the Khun length, \( \xi_0 \) is the correlation length of the polymers.

| reduced viscosity \( \eta_s \) scaling exponent \( \nu \) | \( c < c^* \) | 1 |
| \( c^* < c < c_e \) | 1/2 |
| \( c_e < c < c_D \) | 1.5 \( \pm \) 1.7 |
| \( c > c_D \) | 15/4 |

**TABLE II:** Expected scaling exponents for zero-shear reduced viscosity \[16, 17\] of aqueous polyion solutions in the four typical concentration regimes.

**FIG. 1:** Reduced viscosity \( \eta_s \) as a function of polyion concentration for Na-CMC-90 kD (\( \bigtriangledown \)) and Na-CMC-700 kD (\( \bigcirc \)). The dotted lines represent the expected power laws behaviors according to the different concentration regimes as shown in Tab. III. 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: Reduced viscosity $\eta_s$ as a function of polyion concentration for NaPSS-Mal 20 kD (panel A) and H-PSS 20 kD (panel B). The dotted lines represent the expected power law behaviors according to the different concentration regimes as shown in Tab. 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. The inset in panel A shows the reduced viscosity of Na-PAA (60 kD molecular weight) aqueous solution.

100 mg/ml, in order to completely cover the dilute and semidilute concentration regime) with deionized Q-quality water (Millipore) whose d.c. electrical conductivity was less than $1 \div 2 \mu$mho/cm at room temperature.

B. Electrical conductivity measurements

The electrical conductivity measurements were carried out by means of two Impedance Analyzers Hewlett-Packard mod. 4192A over the frequency range from 40 Hz to 110 MHz and 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. The conductivity cell consists in a short section of a cylindrical coaxial cable connected to the Meter by means of a precision APC7 connector, whose constants have been determined by a calibration procedure with standard liquids of known conductivity and dielectric constant, according to a procedure reported elsewhere [18, 19]. Here, we will deal exclusively with the low-frequency limit of the measured electrical conductivity, obtained by averaging the conductivity values at frequencies below 10 kHz, where only the d.c. contributions are present, being completely negligible the contributions due to the dielectric loss (d.c. conductivity). The behavior of the electrical conductivity as a function of the frequency will be presented and discussed in a forthcoming paper [20].

C. Polyelectrolyte behavior

All the polyion chains have at least one ionizable group per monomer with a mean distance $b$ between charges (Tab. III). In aqueous solution, the charge density pa-
rameter $l_b/b$ is larger than the critical value $(l_b/b = 1)$ and according to the Manning-Oosawa theory [21], counterion condensation will occur. However, it is worth noting that Manning condensation doesn’t apply in extremely dilute polyelectrolyte solutions [22, 23, 24, 25], because of the huge entropy gain occurring when single-chain system passes from a counterion-condensed state to a counterion-uncondensed state.

\[
M_w[kD] \quad N \quad b[A] \quad L_p[\AA] \quad \text{Structure}
\]

|            |       |       |       |                  |
|------------|-------|-------|-------|------------------|
| CMC (I)    | 90    | 400   | 6.87  | 160 rigid        |
| CMC (II)   | 700   | 3200  | 6.87  | 160 rigid        |
| Na-PAa     | 60    | 638   | 2.52  | 7 flexible       |
| H-PAa      | 60    | 638   | 2.52  | 7 flexible       |
| H-PSS      | 75    | 407   | 2.50  | 10 flexible      |
| Na-PSS-Mal | 20    | 103   | 3.30  | 10 flexible      |

TABLE III: Molecular weight $M_w$, degree of polymerization $N$, persistence length $L_p$ (taken from ref. [26, 27, 28]), monomer size $b$ and flexibility properties of the polymers investigated.

IV. RESULTS AND DISCUSSION

The low-frequency electrical conductivity $\sigma$ of the different polyelectrolyte aqueous solutions investigated are shown in Figs. 3 to 5. Measurements extend over a wide range of polyelectrolyte 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 $\sigma$ 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 polyelectrolyte equivalent conductivity, according to the concentration regime and the flexibility of the polyelectrolyte 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 polyelectrolyte conductivity in dilute and semidilute regimes are given by eqs. 6 and 7 where the electrohydrodynamic coefficients are given by eq. 10 for $c < c_c$ and by eq. 11 for $c > c_c$. For rigid polyelectrolytes, we cannot consider the monomer chains as linear sequence of blobs of size $D$ or a sequence of correlation blobs of size $\xi_0$ and we will consider, as simple electrostatic units, the segments of length $b$ and the Kuhn length $l_b$ 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, in which the Kuhn length plays the role of the correlation length $\xi_0$ in the case of more flexible polymers within the semidilute regime.

Eqs. 6 and 7 for the electrical conductivity 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 polyelectrolyte backbone or assumed to be known within the theoretical framework employed. By means of a non-linear 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.

Figs. 6 to 8 show this parameter as a function of polyelectrolyte concentration $c$ for the different polymers 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 [22, 23, 24, 25, 26, 27]. For all the polyelectrolytes investigated and for semidilute (non entangled) regime, $c^* < c < c_c$, a more or less extended plateau is reached and we will name this phase as the Manning regime [22, 23]. 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 $l_b$ [21] according to

\[
f_{th} = 0.886z_1^{-1} \zeta^{-1} \xi = \frac{l_b}{b} \tag{20}
\]

where $z_1$ is the valence of counterions and $\zeta$ is the charge density parameter. While a constant value is observed, its level is significantly lower than the one predicted by Manning (eq. 20).

As far as the CMC polyelectrolytes are concerned, we observe that the level at which the fraction $f$ of free counterions maintains constant, within the semidilute regime, depends on the degree of polymerization $N$. This ef-
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 $f$ value predicted by Oosawa-Manning theory while dotted line is the mean value $\langle f \rangle$ in the Manning regime.

The 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 32, again in sodium polyacrylate salt solution at high concentration 11, 13 and in differently structured compounds of poly(vinyl-benzyl-trialkyl ammonium) chloride or in sodium poly(styrene sulfonate) 22, 23. With the increase of the degree of polymerization, the partial increase of the 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. 6 to 8, has always a lower value than the theoretical prediction (eq. 20). 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 mg/ml and 0.1 mg/ml, respectively.

In the case of flexible polyions, i.e., Na-PAA, H-PAA,
Na-PSS-Mal and H-PSS polions, the conductivity data have been analyzed according to the scaling model of a polion solution and the resulting fraction \( f \) of free counterions is shown in Figs. 7 and 8. 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 polions.

For the sake of completeness, we remark that if we had extended the Manning model to flexible polions (either considering a sequence of subunits of length \( b \) or a sequence of subunits of length \( l_k \)), an inconsistence 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 polion solution) in the case of flexible polions.

A final comment is in order. In the case of rigid polions, 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, wouldn’t have been sensibly different from the ones obtained (Fig. 6) considering a change in the length scale of basic electrostatic unit from the monomer length \( b \) to the Khun length \( l_k \). This result furnishes further support to the analysis of conductivity data employing different models in consequence of different conformation of the polion 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 [7, 33], we present, for a series of differently flexible polion solutions, how the fraction of free counterions, due to the counterion condensation, varies with the polion concentration. These results offer further support to the fact that the effective charge of a polion 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 [34]. On the other hand, for all the polions investigated, the dilute regime is characterized by monotonic decrease of free counterion fraction as polion concentration is increased in accordance with previous theoretical results [23, 24] that strongly underly the importance of entropic effects at infinite dilution.

The influence of the different flexibility chain effects have been taken into account using the scaling blob model [10] to analyze flexible chains (Na-PAA, H-PAA, H-PSS and Na-PSS-Mal polions) and a simple Manning scheme for rigid polions (CMC-90 kD and CMC-700 kD). At high concentration regime, for \( c > c_c \) and for all polions 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 can not 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 polions in good solvent condition, but it could be extended to polions in poor solvent conditions, where a strong re-structuring of the polion chain within the necklace model [4] is expected. These investigations may give useful information on the conformation of a polion 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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