

Electrical Conductivity of Dilute and Semidilute Aqueous Polyelectrolyte Solutions. A Scaling Theory Approach

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We study the low-frequency electrical conductivity of flexible charged polymer chains in salt-free aqueous solutions on the basis of the Manning counterion condensation model, taking into account a dynamic scaling description recently proposed by Dobrynin, Colby, and Rubinstein (*Macromolecules* **1995**, 28, 1859) of the polyion configuration in different concentration regimes covering both the dilute and semidilute regions. We compare the prediction of this model with conductivity data obtained for salt-free aqueous solutions of poly(L-lysine) of four different molecular weights (from 4 to 167 kD), over an extended concentration interval to cover the different regimes, from dilute to semidilute unentangled solutions. Our predictions are found to compare favorably well with the observed conductivity behavior over the whole concentration range investigated.

1. Introduction

Aqueous solutions of charged polyions behave differently from those of uncharged polymer ones, owing to the large counterion atmosphere in the immediate vicinity of the polyion itself that influences a variety of transport and colligative properties. Polyelectrolytes are macromolecules that in aqueous solution carry a large number of charged groups, and the strong cooperative interaction between them and counterions, deriving from the ionization of their charged groups, determines the nonideal behavior of these systems.^{1–3} Moreover, current interest in charged polymer solutions, in particular in high-molecular weight ionic macromolecules, is also supported by the needs of biophysics since biopolymers are usually charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behavior.⁴

The description of different electrical properties of polyions in aqueous solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory^{5–8} that, under some aspects, can be considered equivalent to the Poisson–Boltzmann cylindrical cell model.^{9–13} Within this model, the polyion is represented as an infinitely long charged line, small ions (counterions) are assumed to form an ionic atmosphere whose density depends on the frame of the polyion and their interactions with the charged polyions groups are purely Coulombic, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye–Hückel approximation. The solvent is assumed to be a continuous medium characterized by a spatially uniform

dielectric constant ϵ . Interactions among polyions are neglected, the theory being addressed to highly diluted solutions. On the basis of these assumptions, this approach has been successfully applied to different polyelectrolyte systems, and numerous experiments have strongly suggested the validity of this model.^{14–20}

Because Manning counterion condensation theory deals only with polyelectrolyte solutions in a highly diluted regime, its applicability to dilute or semidilute systems cannot be easily done, especially when the polyion concentration modifies the flexibility of the chain, giving rise to different conformational aspects. We shall limit our approach to the electrical conductivity σ , which represents a significative parameter in the characterization of charged polymer solutions since it has long been recognized as an effective measure of the movement of any charged unity under the influence of an external electric field.

In this work, we describe the electrical conductivity of a polyelectrolyte solution in the dilute and semidilute regimes on the basis of the Manning counterion condensation theory, taking into account a scaling description of the configuration of both dilute and semidilute unentangled polyelectrolyte chains in salt-free solutions, recently proposed by Rubinstein, Colby, and Dobrynin,^{21,22} based on scaling theories of de Gennes et al.^{23,24}

The conductivity σ of the brome salt of poly(L-lysine) of different molecular weights has been measured in a wide polyion concentration range, up to about 12 mg/mL, to cover the whole dilute region, and the influence of the polyion conformation on the electrical transport properties has been discussed using a simple scaling model of polyelectrolyte solution that allows the Manning formalism to be extended to more concentrated

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systems. The present theory clearly demonstrates the significance of the polyion chain conformation on the polyion mobility, particularly in polyelectrolyte solutions without added salt.

2. Theoretical Approach

2.1. Manning Counterion Condensation Theory (a Review). The counterion condensation theory represents a polyion chain of contour length l by a linear array (infinitely thin or having finite thickness) of N monomers, each of them bearing a charge $|z_p|e$ with counterions of charge $|z_1|e$ partially condensed onto the polyion and partially noncondensed and distributed in the neighborhood of the polyion (polyelectrolyte cell model) according to the linearized Poisson–Boltzmann equation.^{13,25} In the limit of very high dilution (neglecting any interaction between polyions), the conductivity behavior of the whole solution is characterized by a charge-density parameter ξ , defined as

$$\xi = \frac{e^2}{\epsilon k_B T b} \quad (1)$$

where e is the electronic charge, ϵ is the dielectric constant of the aqueous phase, $k_B T$ is the thermal energy, and $b = l/N$ is the average spacing between charged groups on the polyion chain.

When ξ exceeds the critical value $\xi_c = 1/|z_1 z_p|$, where z_1 and z_p are the valences of free counterions and polyion charged groups, respectively, a fraction

$$(1 - f) = 1 - \frac{1}{|z_1 z_p| \xi} \quad (2)$$

will condense on the polyion chain to reduce its effective charge to a critical value corresponding to ξ_c . On the other hand, when ξ is lower than ξ_c , condensation does not occur and the polyion has the really linear charge density $z_p e/b$, the counterion concentration equals its stoichiometric value, and the counterions are distributed over the whole volume of the solution.

The electrical conductivity σ of a dilute charged polyion solution based on simple additivity of contributions of the charged entities (counterions, ions from added salt, polyions) present in the solution, can be written as

$$\sigma = \sum_i c_i \lambda_i \quad (3)$$

where c_i and λ_i are the concentrations (in equivalent cm^{-3}) and the equivalent ionic conductivities (in $\Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$) of the i th charge carrier, respectively. In the absence of added salt and in the presence of ion condensation ($\xi > 1/|z_p z_1|$), eq 3 reads

$$\sigma = c_1 \lambda_1 + c_p \lambda_p \quad (4)$$

where $c_1 = N_p N / |z_1| \xi$ is the concentration of free counterions, $c_p = N_p N / |z_1| \xi$ is the concentration of fixed charge on the polyion chain, λ_1 and λ_p are the equivalent ionic conductance of counterions and polyions, respectively, and finally, N_p is the concentration (in mol cm^{-3}) of polyions. In the following, attention will be restricted to monovalent charged groups and mobile ions.

According to Manning, the counterion equivalent conductance λ_1 is related to the limiting equivalent ionic conductance λ_1^0 (in the absence of polyion) through the relation

$$\lambda_1 = \lambda_1^0 \frac{D_1^u}{D_1^0} - \lambda_p \left(1 - \frac{D_1^u}{D_1^0} \right) \quad (5)$$

where D_1^u/D_1^0 is the ratio of the self-diffusion coefficients of free counterions (uncondensed) in the polyelectrolyte solution in the presence and in the absence of the polyion, respectively. Numerical evaluation of this quantity given in refs 5 and 6 yields a value $D_1^u/D_1^0 \approx 0.866$. Finally, eq 4 becomes

$$\sigma = \frac{NN_p}{\xi} \frac{D_1^u}{D_1^0} (\lambda_1^0 + \lambda_p) \quad (6)$$

The equivalent conductance λ_p of the polyion has been derived by Manning⁸ in the context of the model for counterion condensation theory, taking into account a “charged solvent” effect due to counterelectrophoresis and an “asymmetry field” effect due to the distortion of the Debye–Hückel ion atmosphere exerted by the external electric field.

For $\xi > 1/|z_1 z_p|$, the polyion equivalent conductance λ_p is given by

$$\lambda_p = \frac{F}{300} \frac{\frac{D_1^u}{D_1^0} Q_{\text{tot}}}{\left(1 - \frac{D_1^u}{D_1^0} \right) \frac{Q_{\text{tot}}}{u_1^0} + \frac{3\pi\eta N b}{|\ln(K_D b)|}} \quad (7)$$

where F is the Faraday constant ($F \approx 96\,500 \text{ C mol}^{-1}$), u_1^0 is the counterion mobility in the aqueous phase without polyions, $Q_{\text{tot}} = Ne/\xi$ is the effective charge (after condensation) on the polyion chain, and K_D is the inverse of the Debye screening length, given by

$$K_D = (4\pi b N N_p N_A)^{1/2} \quad (8)$$

where N_A is the Avogadro number.

It is noteworthy that the Manning theory does not contain any adjustable parameter and, despite its simplicity, has been rather successful in explaining various colligative properties of polyelectrolyte solutions. Since the Manning theory applies, as above stated, to highly diluted solution (any polyion–polyion interaction is neglected) and to polyions modeled as a linear array of point charges, its validity is confined to very low concentration polyelectrolyte solutions.

In the following section, we will try to extend its applicability to more concentrated systems, on the basis of the scaling picture for the conformation of a polyelectrolyte chain in the dilute and semidilute regimes in a salt-free solution.

2.2. Scaling Theory of Polyelectrolyte Solutions (Dobrynin, Colby, and Rubinstein^{21,22}). Recently, Dobrynin, Colby, and Rubinstein,²¹ extending the scaling picture of de Gennes et al.²⁴ and Odijk,²⁶ describe the configuration of a salt-free intrinsically flexible polyelectrolyte solution in either the dilute or semidilute regime. These authors consider a polyelectrolyte solution with $c = (NN_p N_A)$ monomer per unit volume of charged flexible chains and point out that there are two different polyion concentrations that correspond to two scale lengths, the interaction concentration c_{int} , at which the Debye screening length $1/K_D$ equals the distance $R_M \approx (N/c)^{1/3}$ between polyion chains and the overlap concentration c^* , for which the distance R_M is equal to the extended size L of the chain. We briefly review here, using the notation of Dobrynin et al.,²¹ the main features of these different configurations.

At very low polyion concentration (dilute regime), $c < c_{\text{int}}$, the Debye screening length $1/K_D$ is much larger than the distance between chains and charges interact via the unscreened Coulombic potential. Each polyion, extended in a rodlike configuration, can be represented as a chain of electrostatic blobs of average size D , containing g_e monomers. The statistics of the chain inside the electrostatic blob is determined by the thermodynamic interaction between uncharged polymers and solvent.^{21,22} Each blob bears a charge $q_D = (g_e/A)e$, where A is the average number of monomers per effective charge, thus incorporating the effect of counterion condensation. On length scales larger than D , the $N_D = N/g_e$ blobs of each chain repel each other to form a fully extended chain of length $L = N_D D = (N/g_e)D$. At higher concentrations, $c_{\text{int}} < c < c^*$, the system behaves as a dilute solution of weakly interacting chains. In this case, the electrostatic screening length is no more $1/K_D$, but $r_{\text{scr}} \approx R_M \approx (N/c)^{1/3} > 1/K_D$. The polyelectrolyte chain is still extended with an end-to-end distance L .

At concentrations higher than the overlap concentration c^* , $c > c^*$ (semidilute regime), there exists a correlation length ξ_0 that in this regime is identical to the screening length and that defines two different types of chain behavior. On length scales shorter than ξ_0 , the chain conformation is similar to that in dilute solutions and the chain is a fully extended conformation of electrostatic blobs. On length scales longer than ξ_0 , the chain has random walk statistics, the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs. The derivation of an expression for the electrical conductivity in dilute and semidilute polyelectrolyte solutions proceeds following the Manning treatment, taking into account the transport process in an external electric field as influenced by both polyion-solvent and polyion-counterion interactions.

2.2.1. Dilute Solutions, $c < c_{\text{int}} \approx c^*$. According to the treatment of Manning,⁸ the calculation of the electrical conductivity takes into account the effects due to hydrodynamic interactions (both between a simple structural unit and pure solvent and between different units of the same polyion) and those due to the asymmetry field.

In this case, the simple structural unit is the electrostatic blob of size D and charge $q_D = (g_e/A)e$ and the friction coefficient is given by

$$\zeta = 3\pi\eta D \quad (9)$$

where η is the viscosity of the solvent.

The electrophoretic friction coefficient, including hydrodynamic interactions, according to the general expression given by Kirkwood,²⁷ can be written as

$$f_E = \frac{N_D \zeta}{1 + \frac{\zeta}{6\pi\eta N_D} \sum_i \sum_{j \neq i} \langle r_{ij}^{-1} \rangle} \quad (10)$$

where $N_D = N/g_e$ is the number of electrostatic blobs in each chain and r_{ij} is the distance between two blobs.

It must be noted that in the Manning theory, r_{ij} is the distance between point charges i and j regarded as point sources of friction, whose maximum value (the contour length Nb) is larger than the Debye screening length $1/K_D$:

$$(r_{ij})_{\text{max}} \approx Nb > 1/K_D \quad (11)$$

In this case, r_{ij} is the distance between blobs i and j and the following condition holds:

$$(r_{ij})_{\text{max}} \approx N_D D = \left(\frac{N}{g_e}\right)D < 1/K_D \quad (12)$$

Let $r_{ij} = |i - j|D$. Due to the extended configuration of the electrostatic blob chains, we have

$$D < r_{ij} < (N_D - 1)D < 1/K_D \quad (13)$$

and the average term in eq 10 must be calculated with a cutoff function $\exp(-hr_{ij})$, with $h^{-1} \sim N_D D$, in order to neglect contributions for $r_{ij} > N_D D$. It follows that

$$\begin{aligned} \sum_i \sum_{j \neq i} \langle (r_{ij})^{-1} \rangle &\approx \frac{1}{D} \sum_i \sum_{j \neq i} \frac{\exp(-hD|i-j|)}{|i-j|} \approx \\ &\frac{2N_D}{D} \sum_{|i-j|=1}^{N_D-1} \frac{\exp[-(h|i-j|D)]}{|i-j|} \approx \frac{2N_D}{D} |\ln(hD)| \end{aligned} \quad (14)$$

with the conditions $hD \approx 1/N_D \ll 1$, $N_D \rightarrow \infty$. Thus, eq 10 results

$$f_E = \frac{N_D \zeta}{1 + \frac{\zeta |\ln(hD)|}{3\pi\eta D}} \approx \frac{3\pi\eta N_D D}{\ln N_D} \quad (15)$$

Since we put $h^{-1} \approx N_D D$, this equation holds in the limit that the cutoff of the hydrodynamic interaction is the fully extended length of the electrostatic blobs, rather than the Debye screening length $1/K_D$.

By comparing eq 15 with the analogous one given by Manning, we note that the denominator is independent of K_D (and thus of the ionic strength) and of the size of the blobs, but it depends weakly on their concentration, i.e., on the ratio N/g_e .

According to Manning, the total electrophoretic friction coefficient, corrected for the asymmetry field, is given by

$$(f_E)_{\text{tot}} = \frac{f_E}{1 - \frac{\Delta E_p}{E}} \quad (16)$$

where the total asymmetry field acting on the polyion depends on the charge $Q_T = Ne/A$ according to

$$\frac{\Delta E_p}{E} = \left(1 + \frac{Q_T}{(f_E)_{\text{tot}} u_1^0}\right) \left(1 - \frac{D_1^u}{D_1^0}\right) \quad (17)$$

and the equivalent conductance λ_p of the polyion is given by

$$\lambda_p = \frac{F Q_T}{300 (f_E)_{\text{tot}}} = \frac{F}{300} \frac{\frac{D_1^u}{D_1^0} Q_T}{\left(1 - \frac{D_1^u}{D_1^0} \frac{Q_T}{u_1^0} + \frac{3\pi\eta N_D D}{\ln N_D}\right)} \quad (18)$$

In the absence of added salt, eq 4 holds, and the electrical conductivity of the whole solution is now given by

$$\sigma = \frac{N_p N}{A} \frac{D_1^u}{D_1^0} (\lambda_1^0 + \lambda_p) \quad (19)$$

where λ_p is given by eq 18. For concentrations $c_{\text{int}} < c < c^*$, we expect that equation 19 is still valid, because polyelectrolyte

chains in a salt-free dilute solution are always extended with end-to-end distance L .

2.2.2. Semidilute Solutions, $c > c^*$. In this concentration regime ($c > c^*$), the polyion chain is a random walk of $N_\xi = N/g$ correlation blobs, each of them of size ξ_0 , containing g monomers. Although in this regime the Manning theory does not hold, the strong analogy with the scaling description of Dobrynin et al.²¹ deserves some comments. Whereas in the Manning theory for $r_{ij} \gg 1/K_D$ the electrostatic interactions are completely screened and for $r_{ij} \sim 1/K_D$ the polyion assumes a fully extended configuration, in the scaling theory, for $D < r < \xi_0$ the electrostatic interactions dominate and the chain is a fully extended conformation of electrostatic blobs of size D and for $r > \xi_0$ the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

The electrophoretic friction coefficient f_E when hydrodynamic interactions are included, according to the general expression given by Kirkwood²⁸ for a random coil chain of N_ξ spherical correlation blobs of size ξ_0 and friction coefficient ζ is given by

$$f_E = \frac{N_\xi \zeta}{1 + \frac{\zeta}{6\pi\eta N_\xi} \sum_i \sum_{j \neq i} \langle (r_{ij})^{-1} \rangle} = \frac{N_\xi \zeta}{1 + \frac{8\sqrt{N_\xi}}{3} \frac{\zeta}{(6\pi^3)^{1/2} \eta \xi_0}} \quad (20)$$

The friction coefficient f_E has been evaluated on the assumption that, even in semidilute regime, monomer–monomer interactions within the same chain dominate interactions between monomers on neighboring chains. The friction coefficient ζ associated with a single rodlike unit of size ξ_0 , formed by $N_D/N_\xi = g/g_e$ spheres of size D , can be written as²⁹

$$\zeta = \frac{3\pi\eta\xi_0}{\ln(g/g_e)} \quad (21)$$

and taking into account the effect of asymmetry field (eq 16) and the total asymmetry field function acting on the polyion (eq 17), the polyion equivalent conductance λ_p is given by

$$\lambda_p = \frac{FQ_T}{300(f_E)_{eff}} = \frac{F \frac{D_1^u}{D_1^0} Q_T}{300 \left[f_E + \left(1 - \frac{D_1^u}{D_1^0} \right) \frac{Q_T}{u_1^0} \right]} \quad (22)$$

where $Q_T = Ne/A$ and f_E is given by eq 20.

As a final result, the electrical conductivity according to eq 4 is given by

$$\sigma = \frac{N_p N D_1^u}{A D_1^0} (\lambda_1^0 + \lambda_p) \quad (23)$$

where λ_p is given by eq 22.

In the present case, in both the dilute and semidilute regime, the evaluation of the term D_1^u/D_1^0 in eq 19 and eq 23 requires some comments. Following the derivation given by Manning,⁶ the ratio D_1^u/D_1^0 can be expressed in terms of the Fourier components of the electrostatic potential set up by the fixed polyions. These components, in the Manning picture, depend on the polyion charge density e/b and on the concentration of

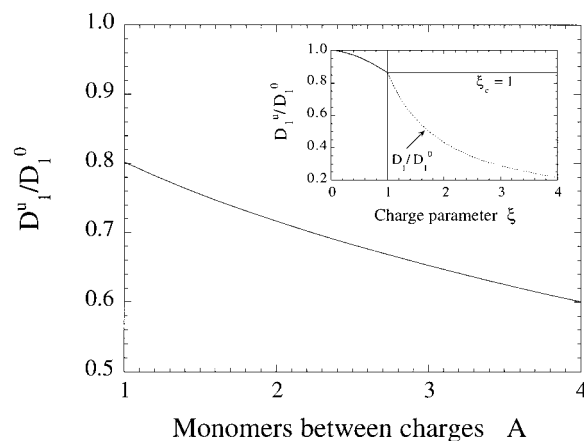


Figure 1. Counterion self-diffusion coefficient ratio D_1^u/D_1^0 according to eq 25 as a function of the number A of monomers between charges on the polyion chain in the case $b = 3.4$ Å. Values of $A > 1$ indicate counterion condensation. The inset shows the counterion self-diffusion coefficient ratio in the Manning model, in absence ($\xi < 1$) and in presence ($\xi > 1$) of counterion condensation.

uncondensed counterion density n_1 that, in the scaling picture, must be replaced with $Q_D/D = g_e e/AD$ and c/A , respectively, yielding the following expression

$$\frac{D_1^u}{D_1^0} = 1 - \frac{1}{3} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \left[\frac{\pi AD}{l_B g_e} (m_1^2 + m_2^2) + 1 \right]^{-2} \quad (24)$$

where $l_B = e^2/(\epsilon K_B T)$ is the Bjerrum length and $(m_1, m_2) \neq (0, 0)$. Taking into account the dependences given by Dobrynin et al.^{21,22} for the blob size D and the number of monomers g_e inside a blob, we obtain, in the case of a poor solvent

$$\frac{D_1^u}{D_1^0} = 1 - \frac{1}{3} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \left[\pi \left(\frac{l_B A}{b} \right)^{-1/3} (m_1^2 + m_2^2) + 1 \right]^{-2} \quad (25)$$

Numerical evaluation of eq 25 as a function of A , in the case $b = 3.4$ Å is shown in Figure 1. These values differ from those given by Manning,⁶ mainly in the counterion condensation region, where at a constant value $D_1^u/D_1^0 \approx 0.866$ for $\xi > 1$, it corresponds, starting from about $D_1^u/D_1^0 \approx 0.800$, to a continuously decreasing value as the parameter A increases, i.e., as the condensed counterion concentration increases. Both eqs 19 and 23, respectively, for $c < c_{int} \approx c^*$ and $c > c^*$, have a single free parameter, the average number A of monomers per effective charge, which gives the fraction of condensed counterions that effectively screens the polyion charge.

3. Experimental Section

Four different samples of poly(L-lysine) (PLys) hydrobromide, $(C_6H_{12}N_2O-HBr)_n$, were obtained from Sigma Chemical Co. The molecular weights reported by the manufacturer were 4, 18, 100, and 167 kDa.

All the solutions were prepared at the desired polymer concentration (within the range from $C = 0.5$ mg/mL to $C = 12$ mg/mL) with deionized Q-quality water (Millipore), whose electrical conductivity was less than $(1 - 2) \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 20 °C. The pH of the solutions, in the polymer concentration and temperature intervals investigated, varied between 7.80 and

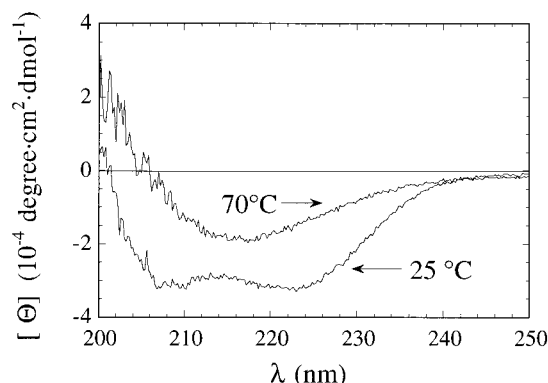


Figure 2. Circular dichroism spectra of poly(L-lysine) aqueous solutions for two different temperatures, at basic pH (pH = 11). The bands at 205 and 222 nm are typical of an α -helix structure ($T = 25$ °C). At higher temperatures ($T = 70$ °C), the spectrum corresponds to the β -sheet conformation.

8.00. At these pH values, the polymer is fully ionized and behaves as a polyelectrolyte, having a charged group per monomer with a monomer length $b = 3.4$ Å. In aqueous solutions, the charge density parameter ξ is larger than the critical value $\xi_c = 1/|z_1 z_p|$ and, according to the Manning theory, counterion condensation is expected.

The polymer concentration, for the four different molecular weights investigated, has been varied to completely cover the dilute up to the semidilute region. For each polymer solution, at a given concentration, the temperature has been varied from 5 to 50 °C, within 0.2 °C.

The electrical conductivity σ was obtained from standard impedance measurements carried out by means of an impedance analyzer (Hewlett–Packard model HP 4192A). The conductivity cell consists of two platinum electrodes 1 mm apart covered with platinum black, whose constants have been determined by calibration with standard liquids of known conductivity and dielectric constant, based on the procedure proposed by Bottomley.³⁰ The accuracy in the conductivity measurements is about 0.3%.

In order to check the integrity of the poly(L-lysine) samples we have investigated by means of electrical conductivity measurements, circular dichroism spectra were recorded in solutions at basic pH (pH = 11). For all the samples investigated at 25 °C, dichroism spectra typical of an α -helix structure were obtained, with two dichroic bands at 222 and 205 nm, corresponding to $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively (Figure 2). At a higher temperature ($T = 70$ °C), the spectrum corresponds to the β -sheet conformation.

4. Results and Discussion

The electrical conductivity of aqueous solutions of poly(L-lysine) at different selected temperatures between 10 and 50 °C are shown in Figures 3–6 as a function of polyion concentration, for the four molecular weights investigated. As can be seen, in all the experimental conditions studied, the conductivity varies linearly with the polyion concentration C .

To compare experiments with theory (eq 19 and/or eq 23, according to the dilute or semidilute regime), we need to know the overlap concentration c^* for the polymer chain investigated. According to the relations given by Dobrynin et al.,²¹ the overlap concentration c^* (expressed in monomers per unit volume) is determined by the relation

$$c^* \approx B^3 b^{-3} N^{-2} \quad (26)$$

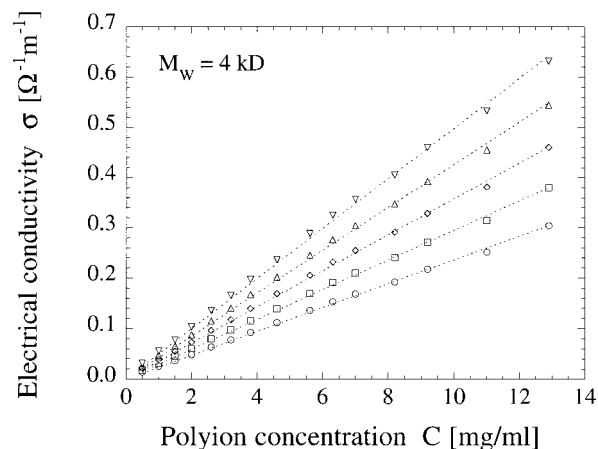


Figure 3. Electrical conductivity σ of poly(L-lysine) in salt-free aqueous solution as a function of polymer concentration at some selected temperatures: (○) $T = 10$ °C; (□) $T = 20$ °C; (◇) $T = 30$ °C; (△) $T = 40$ °C; (▽) $T = 50$ °C. The polyion molecular weight is $M_w = 4$ kDa. The dotted lines represent the calculated values according to eq 19 (dilute regime, $c < c^*$).

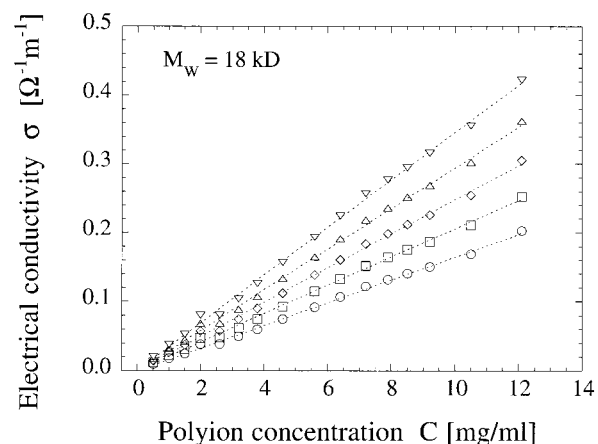


Figure 4. Electrical conductivity σ of poly(L-lysine) in salt-free aqueous solution as a function of polymer concentration at some selected temperatures: (○) $T = 10$ °C; (□) $T = 20$ °C; (◇) $T = 30$ °C; (△) $T = 40$ °C; (▽) $T = 50$ °C. The polyion molecular weight is $M_w = 18$ kDa. The dotted lines represent the calculated values according to eq 19 (dilute regime, $c < c^*$).

where the parameter B , defined as the ratio of the chain contour length Nb and the fully extended chain length L of electrostatic blobs, assumes, in a poor solvent, approximately the value

$$B \approx (A^2 b / l_B)^{2/3} \quad (27)$$

This definition of c^* agrees with that calculated on the basis of the spherical (or cylindrical) cell model as the concentration at which the average distance R_M between polyions equals their extended length $N_D D$.

The numerical evaluation of the concentration c^* depends on the parameter B . Assuming B of the order of 4–5, we obtain values of c^* of the order of 3×10^{18} and 1×10^{19} monomers/cm³, corresponding to a crossover concentration of 1 and 4 mg/mL, respectively, for samples of molecular weight $M_w = 167$ and 100 kDa and values of about $c^* = 3 \times 10^{20}$ and 6×10^{21} monomers/cm³, corresponding to a crossover concentration higher than the maximum concentration investigated ($C = 12$ mg/mL), for samples of molecular weight $M_w = 18$ and 4 kDa. Because the scaling relationships employed to define the crossover concentration deal with unknown prefactors (but of order unity), the assumption $B = 4-5$ must be considered as a

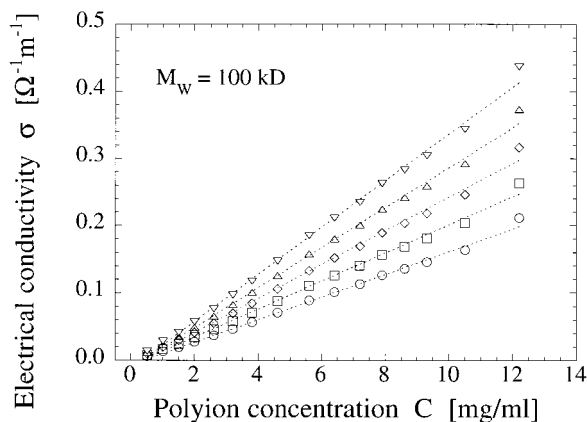


Figure 5. Electrical conductivity σ of poly(L-lysine) in salt-free aqueous solution as a function of polymer concentration at some selected temperatures: (○) $T = 10\text{ }^{\circ}\text{C}$; (□) $T = 20\text{ }^{\circ}\text{C}$; (◇) $T = 30\text{ }^{\circ}\text{C}$; (Δ) $T = 40\text{ }^{\circ}\text{C}$; (▽) $T = 50\text{ }^{\circ}\text{C}$. The polyion molecular weight is $M_w = 100\text{ kDa}$. The dotted lines represent the calculated values according to eq 23 (semidilute regime, $c > c^*$). For this calculation, we analyze data at concentrations exceeding 5 mg/mL , to be certain we are in the semidilute solution regime.

rough estimate. In the case of poly(α -glutamate) aqueous solutions (polymers of molecular weight $M_w = 31\text{ kDa}$), on the basis of the behavior of the dielectric parameters of the high-frequency dielectric dispersions observed in the range 1 MHz to 1 GHz , we have evaluated B to be of the order of $B = 5.5$, yielding a crossover concentration between the dilute and semidilute regimes of the order of $c^* \approx 5 \times 10^{19}\text{ monomers/cm}^3$, corresponding to about $C = 10\text{ mg/mL}$.³¹

Since in this work we have investigated for all the four molecular weights polyion concentrations from 0.5 to 12 mg/mL , our measurements cover completely the dilute regime for samples with $M_w = 4$ and 18 kDa , the semidilute regime for samples with $M_w = 167\text{ kDa}$, and an intermediate regime (with a crossover concentration of about $C \approx 4\text{--}5\text{ mg/mL}$) for samples with $M_w = 100\text{ kDa}$. Correspondingly, we have analyzed our experimental results with eqs 19 and 23 for dilute and semidilute regimes, respectively. As we have above stated, in both these regimes, the measured electrical conductivity increases linearly with the polyion concentration and does not evidence any change in the slope crossing through the overlap concentration c^* . This behavior can be properly evaluated in the case of polyions of molecular weight $M_w = 100\text{ kDa}$, where the overlap concentration is about $C \approx 4\text{--}5\text{ mg/mL}$. To justify the observed behavior, we have plotted in Figure 7 the calculated values of the electrical conductivity for the sample of $M_w = 100\text{ kDa}$ in the dilute regime ($c < c^*$, eq 19) and in the semidilute regime ($c > c^*$, eq 23), on the basis of the predictions of the model we propose. These values compare well, to a first approximation, with a unique linear dependence over the whole concentration interval, as we have experimentally found (see Figures 3–6). A similar behavior of the electrical conductivity has been evidenced by Ito et al.³² in salt-free aqueous solutions of sodium poly(styrenesulfonate).

In Figure 8, we compare the predictions of this model for both the dilute and semidilute regimes (eqs 19 and 23) with those calculated on the basis of the Manning counterion condensation theory (eq 6). To make evident possible deviations between experiment and theory as a function of polymer concentration, we show the polymer equivalent conductances λ_p at two different molecular weights ($M_w = 4\text{ kDa}$ and 167 kDa) calculated on the basis of this model and on the basis of the Manning counterion condensation theory and have compared

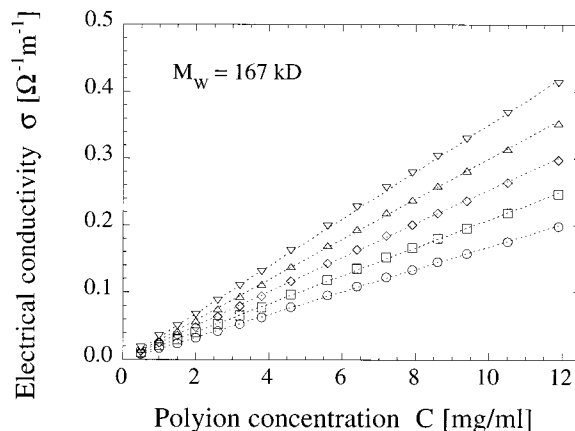


Figure 6. Electrical conductivity σ of poly(L-lysine) in salt-free aqueous solution as a function of polymer concentration at some selected temperatures: (○) $T = 10\text{ }^{\circ}\text{C}$; (□) $T = 20\text{ }^{\circ}\text{C}$; (◇) $T = 30\text{ }^{\circ}\text{C}$; (Δ) $T = 40\text{ }^{\circ}\text{C}$; (▽) $T = 50\text{ }^{\circ}\text{C}$. The polyion molecular weight is $M_w = 167\text{ kDa}$. The dotted lines represent the calculated values according to eq 23 (semidilute regime, $c > c^*$).

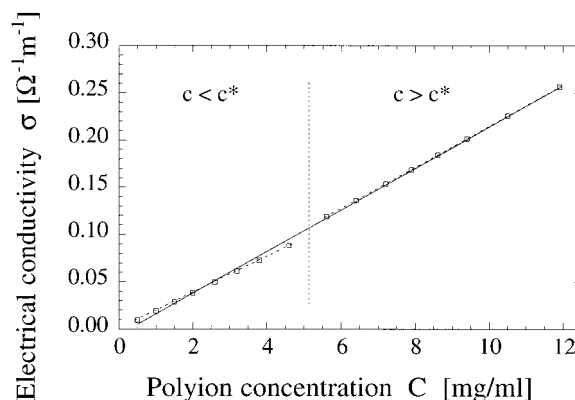


Figure 7. Calculated electrical conductivity values of aqueous solution of poly(L-lysine) of molecular weight $M_w = 100\text{ kDa}$. The dotted lines represent the calculated values on the basis of eqs 19 and 23, according to the different concentration regimes, within the proposed scaling picture. The full line is a linear fit over the whole concentration range.

them with the same quantities derived from the measured electrical conductivity of the whole solution. As can be seen in Figure 8A, Manning theory, whose values are calculated by considering a counterion condensation governed by a charge parameter $\xi = e^2/(\epsilon k_B T b) \approx 2.1$ with $b = 3.4\text{ Å}$, shows remarkable deviations from the expected behavior. Moreover, as pointed out by Manning,⁸ the polyion conductivity is independent of the polymer molecular weight, despite the observed dependence between the lowest and highest molecular weights investigated. On the contrary, a very good agreement is obtained within the scaling theory model. Figure 8, part B, gives an example of this agreement for two different molecular weights. The full results of this analysis are shown in Figure 9, for the four molecular weights investigated, at some selected temperatures. The agreement of theory with the experimental data is particularly significant, considering that the theory contains only one adjustable parameter, the average number A of monomers per effective charges.

From the data shown in Figures 3–6, by means of a fitting procedure, we have determined the parameter A , whose behavior as a function of the polyion molecular weight at some selected temperatures is plotted in Figure 10. For poly(L-lysine) in water the electrostatic blob size $D \approx b(A^2 b/l_B)^{1/3}$ varies between 3.5 and 5.1 Å from lowest to highest molecular weight and the

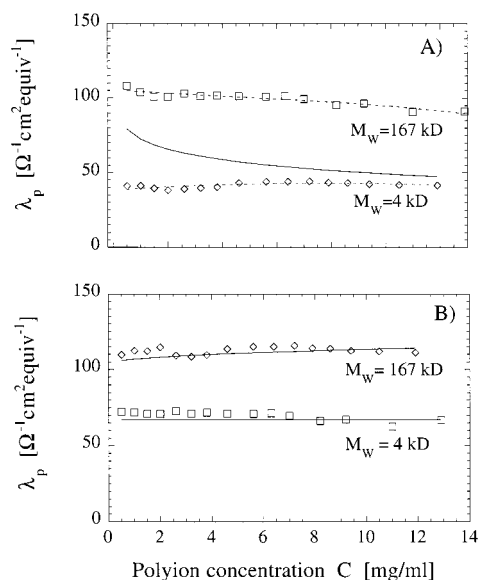


Figure 8. Comparison between the predicted and observed polyion equivalent conductance λ_p on the basis of the Manning counterion condensation theory and on the basis of the scaling theory. (A) Equivalent conductance λ_p calculated on the basis of eq 6 (Manning theory, full line) and the values derived from the measured conductivity within the Manning model: (\square) poly(L-lysine) $M_w = 167$ kDa, $T = 30$ °C; (\diamond) poly(L-lysine) $M_w = 4$ kDa, $T = 30$ °C. The dotted lines represent a polynomial fit to guide the eye only. (B) Equivalent conductance λ_p derived from the measured conductivity on the basis of the scaling theory, according to the dilute regime (eq 19) or semidilute regime (eq 23): (\square) poly(L-lysine) $M_w = 4$ kDa, $T = 30$ °C; (\diamond) poly(L-lysine) $M_w = 167$ kDa, $T = 30$ °C. The full lines represent the calculated values in the two different regimes.

number of effective charges in an electrostatic blob $g_e/A \approx Ab/l_B$ varies from about 0.73 to 1.26, in the same molecular weight range. As can be seen in Figure 10, the parameter A , although close to very few units for all the samples investigated, shows a significant increase passing from low to high molecular weight samples and, to a lesser extent, from lower to higher temperatures.

The values of A of about two to three monomers qualitatively compare with values of $A \approx 5$ found by Dobrynin et al.²¹ in the analysis of measurements of osmotic pressure data of poly(styrenesulfonate) in salt-free aqueous solutions. Recently, Colby et al.,³³ on the basis of the same scaling picture proposed by Dobrynin et al.,²¹ have proposed a simple model of the electrical conductivity for semidilute solutions of strongly charged polyelectrolytes without added salt. Their final result reads

$$\sigma = \frac{NN_p}{A} \left(\lambda_1^0 + \frac{F}{300} \frac{b^{-1}e(A^2/u)^{2/3}}{3\pi\eta A} \ln((NN_p)^{-1/2}b^{-3/2}N_A^{-1/2}) \right) \quad (28)$$

where u is the ratio of the Bjerrum length l_B to the monomer size b , $u = l_B/b$, and N_A is the Avogadro number. These authors, from electrical conductivity measurements of two different polymers in aqueous solutions (sodium salt of poly(styrenesulfonate), $M_w = 1.2$ MDa and sodium salt of poly(2-(acrylamido)-2-methylpropanesulfonate, $M_w = 1.7$ MDa) found a number A of monomers per effective charge close to 4 and to 3, respectively. These values fit well with our finding in the present work for a less flexible polymer chain. In Figure 11, we compare the polyion equivalent conductance λ_p for the poly(L-lysine) samples studied in this work ($M_w = 167$ kDa) derived from eq 28 and the same quantity obtained from the experi-

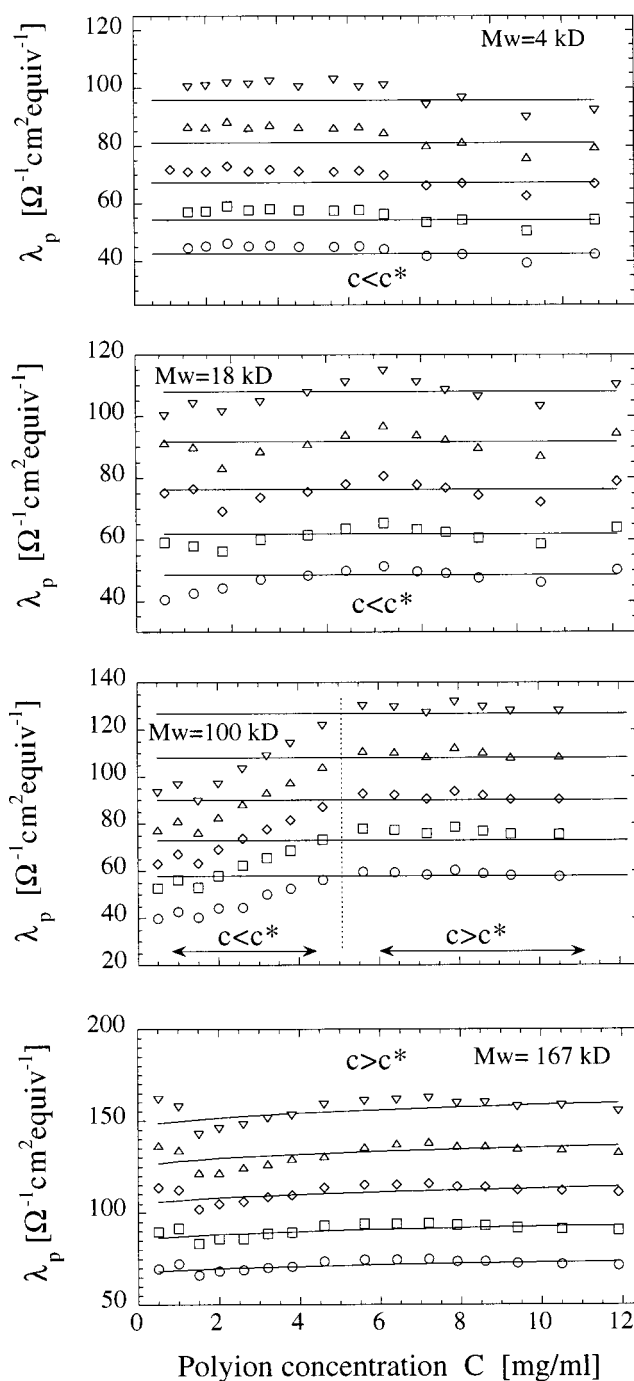


Figure 9. Cumulative plot of the equivalent conductance λ_p derived from the measured electrical conductivity of aqueous solutions of poly(L-lysine) of different molecular weights (from 4 to 167 kDa), at different temperatures: (\circ) $T = 10$ °C; (\square) $T = 20$ °C; (\diamond) $T = 30$ °C; (\triangle) $T = 40$ °C; (∇) $T = 50$ °C. The full lines are the calculated values on the basis of eqs 19 and 23, according to the concentration regime. Deviations occurring with polymer of $M_w = 100$ kDa mean that an intermediate regime prevails, between a dilute ($c < c^*$) and semidilute ($c > c^*$) regime, at approximately a concentration $C \approx 5$ mg/mL.

mental results. As can be seen, the agreement is rather good in the higher concentration range, marked deviations occurring at the lower concentration investigated. Since the theory has been developed in the semidilute regime, these results appear in reasonable agreement with the experiment. It must be noted, however, that the proposed scaling theory accounts for a very good agreement the observed behavior over the whole concentration range we have investigated.

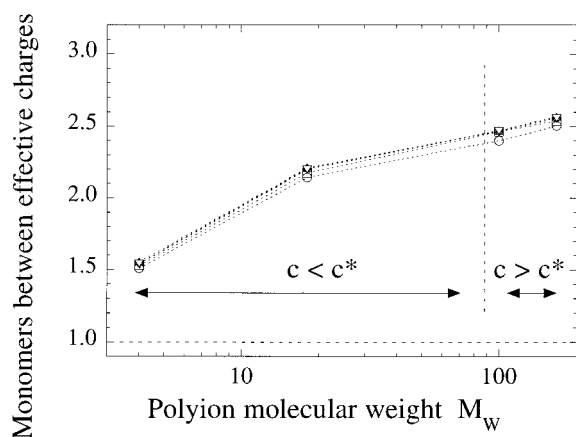


Figure 10. Number A of monomers between effective charges calculated from eqs 19 and 23, according to the different concentration regimes, as a function of the polymer molecular weight, at some selected temperatures: (∇) $T = 10$ °C; (Δ) $T = 20$ °C; (\diamond) $T = 30$ °C; (\square) $T = 40$ °C; (\circ) $T = 50$ °C.

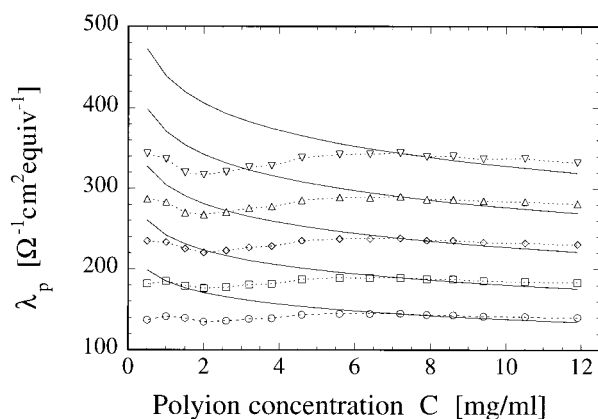


Figure 11. Comparison between the predicted and observed polyion equivalent conductance λ_p on the basis of the conductivity model proposed by Colby et al.³³ The equivalent conductance λ_p is calculated from eq 28 (full lines) and compared with the values obtained from the experimental conductivity, within the Colby model. Calculations are carried out for a polymer of molecular weight $M_w = 167$ kDa at some selected temperatures: (\circ) $T = 10$ °C; (\square) $T = 20$ °C; (\diamond) $T = 30$ °C; (Δ) $T = 40$ °C; (∇) $T = 50$ °C.

5. Conclusions

We have presented a description of the electrical conductivity of flexible polyelectrolytes in aqueous solutions in the dilute and semidilute regimes, where the polymer chain is modeled as an extended configuration of electrostatic or correlation blobs, according to the scaling picture proposed by Dobrynin et al.²¹

Our treatment follows that given by Manning for linear charged polyions in salt-free aqueous solution on the basis of counterion condensation theory and extends those results to higher polyion concentrations in the dilute and semidilute

regime, taking into account two different scale lengths, the size D of the blobs in the dilute region and the correlation length ξ_0 , which defines the chain as a random walk of correlation blobs, in the semidilute region. We have compared the prediction of this model with a new set of data of the electrical conductivity of salt-free aqueous solutions of poly(L-lysine) of different molecular weights in a dilute and semidilute concentration regime. The results are quantitatively consistent with the experimental observations for all the molecular weights investigated.

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