Research Article

Studies of Electrolytic Conductivity of Some Polyelectrolyte Solutions: Importance of the Dielectric Friction Effect at High Dilution

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We present a general description of conductivity behavior of highly charged strong polyelectrolytes in dilute aqueous solutions taking into account the translational dielectric friction on the moving polyions modeled as chains of charged spheres successively bounded and surrounded by solvent molecules. A general formal limiting expression of the equivalent conductivity of these polyelectrolytes is presented in order to distinguish between two concentration regimes and to evaluate the relative interdependence between the ionic condensation effect and the dielectric friction effect, in the range of very dilute solutions for which the stretched conformation is favored. This approach is illustrated by the limiting behaviors of three polyelectrolytes (sodium heparinate, sodium chondroitin sulfate, and sodium polystyrene sulphonate) characterized by different chain lengths and by different discontinuous charge distributions.

1. Introduction

Conductivity is a powerful technique of high accuracy allowing the qualitative and the quantitative detection of ionic species even at low concentrations. On the other hand, it is well known that for electrolytes (or for electrolytes mixtures), it exists a universal linear limiting law relating the equivalent conductivity at high dilution to the square root of ionic strength $I^{1/2}$. This concentration effect is caused by two sorts of ionic frictions: the electrophoretic effect and the ionic relaxation effect. This limiting law has been extended in the case of semidilute simple electrolytes [1–4]. In contrast, a completely satisfactory theory to describe the dynamic behavior in general and particularly the electrolytic conductivity of dilute flexible polyelectrolytes in aqueous solution is not yet available despite some interesting progress toward this objective [5–16]. This difficulty arises from the complex interdependence between polyion conformation, ionic condensation, screening effect, and frictional forces. Moreover, it is important to underline that these different attempts have ignored the influence of the translational dielectric friction on

moving polyions as well as its dependence on concentration [17, 18]. The present paper is a supplementary contribution toward this goal in order to propose a general formal limiting equation expressing the influence of the effects cited above on the equivalent conductivity of polyelectrolytes, and applicable in the range of very dilute solutions for which the stretched conformation is favored and for which the electrophoretic effects and ionic relaxation effects are negligible. This approach will be illustrated by the behaviors of three polyelectrolytes (sodium heparinate, sodium chondroitin sulfate, and sodium polystyrene sulphonate) characterized by different chain lengths and by different discontinuous charge distributions.

2. Theoretical Model and Parameters

2.1. Presentation of the Cylindrical Model. For dilute polyelectrolyte solutions the long chains of ionized polymers are generally assumed to be completely stretched [5–13], so that each chain can be modeled as a cylinder of R_C radius, L_S structural length ($L_S = AB$) and $Z_S e$ structural charge. On

the other hand, as the linear distribution of the total charge $Z_S e$ is uniform, then the distance of separation between two successive ionizable groups is $b_s = L_S/|Z_S|$. Because of the ionic condensation effect, these charged groups are, in absence of additional salt (salt-free), partially neutralized only by counterions “ i ” of $Z_i e$ charge and R_i effective radius. According to Manning’s rod-like model ($R_C/L_S \rightarrow 0$) [6–12], the degree of ionic condensation ($1 - \alpha_M$) is independent on the counterions concentration C_i so that $\alpha_M = b_s/|Z_i|L_B$, where $L_B = e^2/\epsilon_0 k_B T$ is the Bjerrum length, k_B is the Boltzmann constant, and ϵ_0 is the permittivity of the solvent. In fact, experimental conductivity results are not in general in conformity with the current polyelectrolyte theories [10, 11, 14, 15]. In particular, we have proved that for more realistic polyelectrolyte models (rod-like or cylindrical models with finite length and models having ellipsoidal conformations of A, B focuses with $AB = L < L_S$) [9–11], the corresponding degree of dissociation α obeys in general to the Ostwald’s principle of dilution and consequently $\alpha \rightarrow 1$ when $C_i \rightarrow 0$. The degree α was calculated on the basis of the two-state model [10] (double layer) proposed by Séligny, Manning, Dobrynin, and Rubinstein [6–8], but in a different way. According to this approach, the condensed counterions are distributed on an ellipsoidal first layer of A, B focuses and R minor axis, whereas the free counterions constitute the ionic atmosphere which can be represented by an ellipsoidal second layer having the same focuses A, B and a d_p minor axis (see Figure 1). The thickness d_p is a function of R, α and C_i via the Debye-MSA screen parameter Γ_{PMSA} [1] and the Debye length χ_D^{-1} . Notice that both first and second layers are equipotential surfaces of total charges equal, respectively, to $-(1 - \alpha)Z_S e$ and $-\alpha Z_S e$. In the case of the cylindrical model ($AB = L_S, R \equiv R_C$ and $\alpha \equiv \alpha_C$), calculation of α_C needs the resolution of the following ensemble of implicit equations:

$$\frac{(1 - \alpha_C)}{\alpha_C} = (1 - V_P C_P)^{-1} V_P C_P \times \left[\frac{g(R_C, L_S)}{g(d_p, L_S)} \right]^{\{(\alpha_C + |Z_i/Z_S|)/\alpha_M\}}, \quad (1)$$

$$g(x, L_S) = \frac{\left[(4x^2 + L_S^2)^{1/2} + L_S \right]}{\left[(4x^2 + L_S^2)^{1/2} - L_S \right]}, \quad (2)$$

$$d_p = R_C + \frac{1}{2\Gamma_{PMSA}}, \quad (3)$$

$$2\Gamma_{PMSA} = \frac{\left[-1 + (1 + 4\chi_D R_i)^{1/2} \right]}{2R_i}; \quad (4)$$

$$\chi_D = (4\pi L_B Z_i^2 \alpha_C C_i)^{1/2}.$$

C_i and C_P are the microscopic concentrations (number of particles/ $\text{\AA}^3$) of, respectively, the counterions and the polyions. $V_P = \pi R_C^2 L_S$ is the structural volume of the cylindrical polyion. $g(R_C, L_S)$ and $g(d_p, L_S)$ are “the configuration functions” which depend on the conformation of the polyion.

FIGURE 1: Representation of a polyelectrolyte according to the cylindrical model.

Notice first that (1) is a generalization to cylindrical polyions, of the Fuoss expression relative to the ionic association of simple electrolytes; and second, that in the restrictive case of Manning’s model ($R_C/L_S \rightarrow 0$) and for dilute solutions ($R_C/d_p \ll 1$), α_C increases very slowly with dilution so that α_C remains approximately constant in a large range of low concentrations. However, α_C approaches toward α_M only for some particular polyelectrolytes [10].

Notice also that (1) can be applied for ellipsoidal polyions of any shape (i.e., $L \neq L_S, R \neq R_C$ and for all V_P).

2.2. Theoretical Conductivity of Cylindrical Polyelectrolytes in Dilute Solutions. In practice we measure the specific conductance χ of the polyelectrolyte solution in $\text{S}\cdot\text{cm}^{-1}$. χ is related to the equivalent ionic conductivities λ_P and λ_i , respectively, of the polyion and the counterion as follows:

$$\chi = 10^{-3} [\alpha_C |Z_S| \lambda_P C_P^\circ + \alpha_C |Z_i| \lambda_i C_i^\circ], \quad (5)$$

where C_P° is the molar concentration of the polyions and C_i° is the total molar concentration of the counterions so that $\alpha_C C_i^\circ$ is the molar concentration of the free counterions, and $(\alpha_C |Z_S| e)$ is the apparent (effective) charge $|Z_{ap}|e$ of the polyion partially neutralized by the condensed counterions. The electroneutrality condition implies that $|Z_S| C_P^\circ = |Z_i| C_i^\circ$. The equivalent conductivity Λ_{Poly} of the polyelectrolyte is therefore defined by

$$\Lambda_{\text{Poly}} = \frac{1000\chi}{|Z_i| C_i^\circ} = \alpha_C (\lambda_P + \lambda_i). \quad (6)$$

λ_P and λ_i depend on the concentration of the free counterions because of the brake effects on the moving ions (or on polyions) due to their ionic atmosphere. In general one distinguishes two different ionic friction effects [2–4, 9, 12]: (a) the electrophoretic effect which is a hydrodynamic friction on the ionic atmosphere transmitted to the central ion (or polyion) via solvent molecules, (b) the ionic relaxation effect due to the perturbation of the charge distribution of the ionic atmosphere by the external electrical field $\mathbf{E}$. This polarization effect induces on the moving central ion (or polyion) a local field $\Delta \mathbf{X}^{\text{ir}}$ opposed to $\mathbf{E}$. Quantitatively, these

two effects appear in the expression of the ionic conductivity λ_i of *simple* ions (in our case, the counterions) via the $\Delta\lambda_i^{\text{el}}$ corrective term and the β_i^{ir} relaxation term as follows:

$$\lambda_i = \frac{(\lambda_i^\circ - \Delta\lambda_i^{\text{el}})}{(1 + \beta_i^{\text{ir}})}, \quad (7)$$

$$\Delta\lambda_i^{\text{el}} = \left(\frac{|Z_i| Fe}{6\pi\eta d_i} \right); \quad d_i = R_i + \frac{1}{2\Gamma_{\text{MSA}}}, \quad (8)$$

$$\Gamma_{\text{MSA}}^2 \cong \pi L_B \left\{ \left(\frac{(Z_i)^2 \alpha_C C_i}{[1 + 2\Gamma_{\text{MSA}} R_i]^2} \right) + \left(\frac{Z_s^2 \alpha_C^2 C_P}{[1 + 2\Gamma_{\text{MSA}} \langle R_P \rangle]^2} \right) \right\}, \quad (9)$$

$$\langle R_P \rangle = \frac{L_S}{\text{Ln}[g(R_C, L_S)]}. \quad (10)$$

λ_i° is the ionic equivalent conductivity of the counterion at infinite dilution which expresses both the hydrodynamic friction, due to the viscosity η of the solvent (Robinson and Stokes [2]), and the dielectric friction effect (Zwanzig [19]). λ_i° is determined experimentally by linear extrapolation at infinite dilution and according to the Debye-Onsager limiting equation [2], of the equivalent conductivity Λ_{IX} ($\sqrt{I}$) (with the square root of the ionic strength I) of any corresponding simple electrolyte (e.g., if $i \equiv \text{Na}^+$, we can choose $\Lambda_{\text{IX}} \equiv \Lambda_{\text{NaCl}}$; extrapolation of Λ_{NaCl} in water at 25°C leads to $\lambda_{\text{Na}^+}^\circ = 50.1 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$). The term F is the Faraday, R_i is the *effective* radius of the solvated counterion “ i ”, d_i is the radius of its ionic atmosphere, and Γ_{MSA} is its corresponding Debye-MSA screen parameter. Notice that Γ_{MSA} differs from the screen parameter Γ_{PMSA} relating to the polyion, because considering the high repulsion between polyions, we have assumed that the ionic atmosphere of the polyions is constituted only by free counterions; on the contrary, the ionic atmosphere of a counterion encloses both polyions and counterions. $\langle R_P \rangle$ is the mean radius of the polyion (analog to the radius of gyration) which is also equal to the electrostatic capacitance C_{AP} (in c.g.s.u.e units) of the ellipsoidal (or cylindrical) polyion [17, 20]. Finally, the explicit expression of the ionic relaxation term β_i^{ir} will be examined at the end of this section because of its interdependence with the β_P^{ir} term relating to the polyions.

The expression of the equivalent conductivity λ_P of the polyion is more complex because its ionic equivalent conductivity at infinite dilution λ_P° expressing both hydrodynamic friction and dielectric friction effect is experimentally inaccessible. Indeed, in contrast with simple electrolytes, ionic transport behavior of polyelectrolytes is not governed by any universal limiting law [5] allowing the determination of λ_P° by an extrapolation method at infinite dilution. For this reason we decomposed the λ_P expression as follows [9]:

$$\lambda_P = \frac{\lambda_P^{\text{Henry}}}{(1 + \beta_P^{\text{ir}} + \beta_P^{\text{df}})} = \frac{(\lambda_P^{\circ\text{Hyd}} - \Delta\lambda_P^{\text{el}})}{(1 + \beta_P^{\text{ir}} + \beta_P^{\text{df}})}. \quad (11)$$

The justification of the above equation is the following: the external electric field $\mathbf{E}$ acting on the polyion polarizes its ionic atmosphere as well as its surrounding solvent molecules, which gives place to an ionic relaxation field $\Delta\mathbf{X}^{\text{ir}}$ and to a dielectric relaxation field $\Delta\mathbf{X}^{\text{df}}$ slowing down the movement of the polyion. The velocity $\mathbf{v}$ of the polyion can thus be written in two manners:

$$\begin{aligned} \mathbf{v} &= u_P \mathbf{E} = u_P^{\text{Henry}} (\mathbf{E} + \Delta\mathbf{X}^{\text{ir}} + \Delta\mathbf{X}^{\text{df}}) \\ &\equiv u_P^{\text{Henry}} \frac{\mathbf{E}}{(1 + \beta_P^{\text{ir}} + \beta_P^{\text{df}})}. \end{aligned} \quad (12)$$

u_P is the actual electrical mobility of the polyion and u_P^{Henry} is the Henry mobility [9, 21] so that

$$\lambda_P = F u_P; \quad \lambda_P^{\text{Henry}} = F u_P^{\text{Henry}}. \quad (13)$$

β_P^{ir} and β_P^{df} express, respectively, the ionic relaxation effect and the dielectric friction effect acting on the polyion. Equation (12) implies that

$$\begin{aligned} \beta_P^{\text{ir}} &= \frac{|\Delta\mathbf{X}^{\text{ir}}|}{|\mathbf{E} + \Delta\mathbf{X}^{\text{ir}} + \Delta\mathbf{X}^{\text{df}}|}, \\ \beta_P^{\text{df}} &= \frac{|\Delta\mathbf{X}^{\text{df}}|}{|\mathbf{E} + \Delta\mathbf{X}^{\text{ir}} + \Delta\mathbf{X}^{\text{df}}|}. \end{aligned} \quad (14)$$

The explicit expression of the Henry equivalent conductivity λ_P^{Henry} of the polyion is, [9],

$$\lambda_P^{\text{Henry}} = \left(\frac{\alpha_C Fe}{6\pi\eta b_s} \right) \text{Ln} \left[\frac{g(R_C, L_S)}{g(d_P, L_S)} \right]. \quad (15)$$

Accordingly, we can separate λ_P^{Henry} into two contributions: the purely hydrodynamic term $\lambda_P^{\circ\text{Hyd}}$ due to the viscosity η of the solvent, and the so-called electrophoretic term $\Delta\lambda_P^{\text{el}}$, so that

$$\begin{aligned} \lambda_P^{\circ\text{Hyd}} &= \left(\frac{\alpha_C Fe}{6\pi\eta b_s} \right) \text{Ln}[g(R_C, L_S)], \\ \Delta\lambda_P^{\text{el}} &= \left(\frac{\alpha_C Fe}{6\pi\eta b_s} \right) \text{Ln}[g(d_P, L_S)]. \end{aligned} \quad (16)$$

It is remarkable to underline that the expression of $\lambda_P^{\circ\text{Hyd}}$ coincides with the Hubbard-Douglass general relation [20] expressing the hydrodynamic mobility: $u_P^{\circ\text{HD}} \equiv \lambda_P^{\circ\text{HD}}/F$ of an arbitrarily shaped unspecified macroion of $Z_s e$ charge, in terms of its capacitance C_{AP} (generalization of Stokes' law):

$$u_P^{\circ\text{HD}} = \frac{|Z_s| e}{6\pi\eta C_{\text{AP}}}, \quad (17)$$

$$C_{\text{AP}} = \frac{L_S}{\text{Ln}[g(R_C, L_S)]} = \langle R_P \rangle. \quad (18)$$

We can therefore generalize the Hubbard-Douglass relation given by (17) to the Henry equivalent conductivity λ_p^{Henry} as follows [17]:

$$\lambda_p^{\text{Henry}} = \frac{\alpha_C |Z_S| Fe}{6\pi\eta C_{\text{AP}}'} \quad (19)$$

C_{AP}' is now the electrostatic Gouy capacitance (in c.g.s.u.e units) of the ellipsoidal (or cylindrical) capacitor constituted by the polyion and by its ionic atmosphere of mean radius $\langle d_p \rangle$:

$$\left(C_{\text{AP}}'\right)^{-1} = \left[\langle R_p \rangle^{-1} - \langle d_p \rangle^{-1}\right], \quad \langle d_p \rangle = \frac{L_S}{\text{Ln}[g(d_p, L_S)]} \quad (20)$$

Notice that the relative importance of the electrophoretic effect can be evaluated by the ratio:

$$\frac{\Delta\lambda_p^{\text{el}}}{\lambda_p^{\text{Hyd}}} = \frac{\langle R_p \rangle}{\langle d_p \rangle} \quad (21)$$

This last equation implies that the electrophoretic effect vanishes in the range of highly dilute solutions, that is, when $\langle d_p \rangle \rightarrow \infty$. It is also interesting to notice that certain authors [22] have described the electrophoretic mobility of polyions in polyelectrolyte solutions by means of the Debye-Onsager-MSA approach using the mean spherical approximation for the coil conformation of the polyion chain. The corresponding spherical hydrodynamic radius R_H was evaluated according to Stokes-Einstein relation: $R_H = k_B T / 6\pi\eta D_p^\circ$, where D_p° is the self diffusion coefficient of the polyion at high dilution. The same spherical approximation could be used for the calculation of the ionic relaxation effect using Onsager relation applicable to spherical simple ions [3], therefore

$$\beta_p^{\text{ir}} \cong \frac{\alpha_C |Z_i Z_S| L_B q_r^2}{[3(1 + q_r) \langle d_p \rangle]} \quad (22)$$

with: $q_r \cong 1$, if we assume that the ionic atmosphere is free of polyions. However, Manning has demonstrated that for infinite rod-like model ($L_S \gg d_p$), β_p^{ir} remains sensibly constant, equal to 0.13. In order to conciliate the two results into a general expression one of the authors has proposed the following relation [9, 10]:

$$\beta_p^{\text{ir}} = \frac{\alpha_C |Z_S Z_i| L_B (3d_p^2 + L_S^2/4)}{\left[18(d_p^2 + L_S^2/4)^{3/2}\right]}, \quad (23)$$

so that when $L_S/d_p \rightarrow 0$, then $\beta_p^{\text{ir}} \rightarrow \alpha_C |Z_i Z_S| L_B / (6d_p)$; this limiting expression converges toward the Debye-Onsager relation concerning spherical ions. In contrast, for polyions of large length, $L_S \gg d_p$, $\beta_p^{\text{ir}} \rightarrow 1/9$ for all C_i if $\alpha_C \rightarrow \alpha_M$.

On the other hand, according to linear irreversible thermodynamics (T.I.P) the different β_k^{ir} relaxation terms of all the “ k ” species (ions or polyions) in solution are

interdependent via the general relation [9, 14]: $\sum_k Z_k C_k \beta_k^{\text{ir}} = 0$, with $\sum_k Z_k C_k = 0$. This means that in the case of our binary system the two relaxation terms β_p^{ir} and β_i^{ir} , respectively, of the polyions and the counterions are equal:

$$\beta_p^{\text{ir}} = \beta_i^{\text{ir}} \quad (24)$$

Lastly, because of the importance of the dielectric friction effect on a stretched polyion (which is the main subject of this paper) the friction term β_p^{df} will be discussed in detail in the next paragraph.

2.3. Importance of the Dielectric Friction Effect on a Stretched Polyion. The aim of the present paragraph is to evaluate succinctly the frictional force on a slowly moving polyion due to dielectric loss in its surrounding medium. In fact, this dielectric friction effect depends on the conformation (shape) of the polyion. In order to show the link with previous works, we will start by presenting the general formal treatment adopted in all cases; hence we will recall the computation results relating to the spherical and ellipsoidal models. Then, we will treat, without going into the mathematical details, the specific case of a stretched polyion modeled as a chain of $|Z_S|$ identical charged spheres, each one having a charge $q_n = \alpha_C e$ and a radius R_g (a linear discontinuous distribution of ionized groups).

The general mechanism of dielectric friction is the following: when a sphere of charge q and radius R_S is submitted to a moderate external alternating field $\mathbf{E}$ along the z axis, it acquires a velocity $\mathbf{v} = u\mathbf{E}$, where u is its electrical mobility. We indicate by $\mathbf{r}_q(t) = \mathbf{v}t$ the position of the center of the sphere at time t . During its movement the charge q induces at each point M of the dielectric medium (solvent) defined by its radius-vector $\mathbf{r}(x, y, z, t)$ a time-dependent polarization $\mathbf{P}(\mathbf{r}, t)$ which is proportional to the displacement field $\mathbf{D}(\mathbf{r}, t - t_1)$ created by q at different anterior times ($t - t_1$):

$$\mathbf{D}(\mathbf{r}, t - t_1) = \frac{q\mathbf{r}'}{(\mathbf{r}')^3}, \quad \mathbf{r}' = [\mathbf{r}(x, y, z, t) - \mathbf{r}_q(t - t_1)] \quad (25)$$

The module $\mathbf{r}'$ is the distance between the point M and the center of the sphere at time ($t - t_1$). This noninstantaneous response results from the fact that each solvent molecule needs a relaxation time τ to be oriented along the radial field $\mathbf{D}$. Mathematically, the linear relation between $\mathbf{P}(\mathbf{r}, t)$ and $\mathbf{D}(\mathbf{r}, t - t_1)$ is given by the following convolution integral [17, 19]:

$$\mathbf{P}(\mathbf{r}, t) = \left(\frac{1}{4\pi}\right) \int_0^\infty \gamma(t_1) \mathbf{D}(\mathbf{r}, t - t_1) dt_1 \quad (26)$$

with

$$\gamma(t) = \left[1 - \left(\frac{1}{\varepsilon_\infty}\right)\right] \delta(t) + \left[(\varepsilon_0 - \varepsilon_\infty)(\tau\varepsilon_\infty^2)^{-1} \exp\left(\frac{-\varepsilon_0 t}{\varepsilon_\infty \tau}\right)\right] \quad (27)$$

$\gamma(t)$ is the after effect function which depends on the delta function $\delta(t)$ representing electronic relaxation and on the permittivities ϵ_0 and ϵ_∞ , respectively, the static and the high-frequency dielectric constants of the solvent. For water at 25°C, $\epsilon_0 = 78.3$ and $\epsilon_\infty = 1.77$. Note that we have set the upper limit of the above integral to ∞ , because in general the dielectric relaxation time τ is small by comparison to t so that $\gamma(t) \rightarrow 0$ (vanishes rapidly) when $t > \tau$.

In turn, this induced polarization $\mathbf{P}(\mathbf{r}, t)$ exerts back on the charged sphere a resulting dielectric frictional force $\mathbf{F}^{\text{df}} = q\Delta\mathbf{X}^{\text{df}}$ where $\Delta\mathbf{X}^{\text{df}}$ is the so called *dielectric relaxation field* having a direction opposed to the external field $\mathbf{E}$. The general integral relation between the z component ΔX_z^{df} of $\Delta\mathbf{X}^{\text{df}}$ and the D_x , D_y , D_z components of $\mathbf{D}(\mathbf{r}, t - t_1)$ via $\mathbf{P}(\mathbf{r}, t)$ and therefore $\gamma(t_1)$ is, [17],

$$\Delta X_z^{\text{df}} = \left(\frac{1}{4\pi}\right) \int_0^\infty \gamma(t_1) I_z(t_1) dt_1. \quad (28)$$

$I_z(t_1)$ is the so called key integral defined by

$$I_z(t_1) = \iiint \left[\frac{-D_z(t-t_1)}{r'^3} + \frac{3Z^2 D_z(t-t_1)}{r'^5} + \frac{3xZD_x(t-t_1)}{r'^5} + \frac{3yZD_y(t-t_1)}{r'^5} \right] dx dy dz, \quad (29)$$

where $Z = z - vt$. Integration is taken over the whole volume except the *finite* region including the charged sphere (or the polyion in general) from which the dielectric medium is excluded.

It is obvious that no dielectric friction occurs, $\Delta X_z^{\text{df}} \rightarrow 0$ when $\mathbf{v} \rightarrow 0$ (immobile sphere) or when $\tau \rightarrow 0$ (instantaneous response so that $\gamma(t) \rightarrow 0$). In other words, the delay effect ($\tau \neq 0$) causes a perturbation of the equilibrium distribution of solvent molecules around the moving sphere and therefore leads to a nonsymmetrical polarization responsible of the resulting dielectric relaxation field: $\Delta X_z^{\text{df}} \neq 0$. Consequently, linearity between causes and response implies that $\Delta\mathbf{X}^{\text{df}} \sim (\mathbf{v}\tau)$. On the other hand, as the dimension of the electrical relaxation force $\mathbf{F}^{\text{df}} = q\Delta\mathbf{X}^{\text{df}}$ is $\sim (q)^2/[\text{length}]^2$, scaling analysis yields to $\mathbf{F}^{\text{df}} \sim -(q)^2(\mathbf{v}\tau)/R_S^3$.

More rigorous derivations of the expression of the dielectric frictional force on a charged sphere were performed successively by Zwanzig [19], Hubbard and Onsager [23], and Wolynes [24]. In particular, if the charged sphere of large radius R_S is assumed to be a conductor then, hydrodynamic effects become small and all theories reduce to Zwanzig's original result [19] which can be derived from (27) and (28) following the substituting of the explicit expression of $\mathbf{D}(\mathbf{r}, t - t_1)$ given by (25) into (29):

$$\Delta\mathbf{X}^{\text{df}} = \frac{\pm(2q/3)[1 - \epsilon_\infty/\epsilon_0](\mathbf{v}\tau)}{(\epsilon_0 R_S^3)}. \quad (30)$$

We can use the above equation to compute the dielectric friction effect on a spherical polyion of effective charge $q = e\alpha_S Z_S$ and radius R_S . Indeed, according to (12) and (14), its velocity $\mathbf{v}$ is given by $\mathbf{v} = u_p^{\text{Henry}}(\mathbf{E} + \Delta\mathbf{X}^{\text{ir}} + \Delta\mathbf{X}^{\text{df}})$ with $u_p^{\text{Henry}} = \lambda_p^{\text{Henry}}/F$ and the relative dielectric friction effect is defined by $\beta_p^{\text{df}} = |\Delta\mathbf{X}^{\text{df}}|/|\mathbf{E} + \Delta\mathbf{X}^{\text{ir}} + \Delta\mathbf{X}^{\text{df}}|$, therefore (30) leads to $\beta_p^{\text{df}} = (2e\alpha_S|Z_S|/3F)[1 - \epsilon_\infty/\epsilon_0](\lambda_p^{\text{Henry}}\tau)/(\epsilon_0 R_S^3)$. If we explicit the expression of λ_p^{Henry} according to (19) and after replacing the relaxation time τ by its Debye expression in terms of the solvent radius R_w ($R_{\text{H}_2\text{O}} = 1.4$) and the viscosity η so that $\tau = 6\pi\eta R_w^3/k_B T$, we obtain

$$\beta_p^{\text{df}} = \left(\frac{2}{3}\right)(\alpha_C|Z_S|)^2 \left(\frac{R_w}{R_S}\right)^3 \left(\frac{L_B}{C_{\text{AP}}}\right) \left[1 - \frac{\epsilon_\infty}{\epsilon_0}\right]. \quad (31)$$

More recently, authors of [17] have demonstrated that this last expression remains valid even in the case of an ellipsoidal polyion of minor axis R , interfoci distance L , and effective charge $q = e\alpha_E Z_S$ but with the proviso of replacing the spherical radius R_S by an apparent ray R_{app} which is a function of the eccentricity $\gamma = L/2R$ so that $R_{\text{app}} \approx \langle R \rangle$ for $\gamma < 1$ and $R_{\text{app}} \approx L/2$ for $\gamma > 1$.

Now, in the case of stretched chain of $|Z_S|$ successive charged spheres of charge $q_n = -e\alpha_C$ and of radius $R_n = R_g$ ($n = 1, |Z_S|$), each sphere n moving along direction z with velocity $\mathbf{v}_p$ undergoes from the polarized solvent molecules a dielectric frictional force $\mathbf{F}_n^{\text{df}} = q_n \Delta\mathbf{X}_n^{\text{df}}$, where $\Delta\mathbf{X}_n^{\text{df}}$ is the local dielectric relaxation field. Because of the axial symmetry of the system around the z axis, only the z component $\Delta X_{n,z}^{\text{df}}$ of $\Delta\mathbf{X}_n^{\text{df}}$ is different from zero:

$$\Delta X_{n,z}^{\text{df}} = \left(\frac{1}{4\pi}\right) \int_0^\infty \gamma(t_1) I_{n,z}(t_1) dt_1. \quad (32)$$

The corresponding key integral $I_{n,z}(t_1)$ is defined by

$$I_{n,z}(t_1) = \iiint \left[\frac{-D_z(t-t_1)}{r_n'^3} + \frac{3Z_n^2 D_z(t-t_1)}{r_n'^5} + \frac{3xZ_n D_x(t-t_1)}{r_n'^5} + \frac{3yZ_n D_y(t-t_1)}{r_n'^5} \right] \times dx dy dz. \quad (33)$$

x , y , and Z_n are the components of the vector $\mathbf{r}_n'$ separating a point $M(x, y, z)$ of the dielectric medium and the position of the charge q_n at time $(t - t_1)$. The principal difference between (25)–(29) relating to a spherical polyion and (32) and (33), comes primarily from the fact that the expression

of the displacement field $\mathbf{D}(\mathbf{r}, t - t_1)$ created by the stretched chain of charged spheres at $M(x, y, z)$ is now

$$\mathbf{D}(\mathbf{r}, t - t_1) = \frac{q_n \mathbf{r}_n'}{(r_n')^3} + \sum_{i \neq n}^{|Z_S|-1} \mathbf{D}_i(\mathbf{r}, t - t_1), \quad (34)$$

$$\mathbf{D}_i(\mathbf{r}, t - t_1) = \frac{q_i \mathbf{r}_i'}{(r_i')^3}.$$

This equation results from the principle of superposition so that (34) differs from (25) by the sum $\sum \mathbf{D}_i(\mathbf{r}, t - t_1)$ expressing the interference of the displacement field $\mathbf{D}_n(\mathbf{r}, t - t_1)$ created at M by q_n at an anterior time $(t - t_1)$, with the different $\mathbf{D}_i(\mathbf{r}, t - t_1)$ due to the $(|Z_S| - 1)$ charges q_i of the moving chain. Notice however that, if the distance: $b_S = L_S/|Z_S|$, between two successive charged groups, is sufficiently large ($b_S \gg 2R_g$, i.e., $f = b_S/R_g \gg 2$) so that: $r_i' > r_n'$, then the dielectric friction undergone by the sphere q_n is essentially due to polarized solvent molecules of its entourage. We could therefore neglect the interference effect and $\mathbf{D}(\mathbf{r}, t - t_1)$ is reduced thus to $\mathbf{D}_n(\mathbf{r}, t - t_1) = q_n \mathbf{r}_n' / (r_n')^3$; in other words, each charged sphere of the moving polyion of radius R_g and charge $q_n = -e\alpha_C$ behaves as if it were alone to polarize the dielectric medium. Consequently, simple direct application of Zwanzig's original result leads by analogy to (31) to the following obvious equation:

$$\beta_P^{\text{df}} = \left(\frac{2}{3}\right) \alpha_C^2 \left(\frac{R_w}{R_g}\right)^3 \left(\frac{L_B}{b_S}\right) \left(\frac{L_S}{C_{\text{AP}}'}\right) \left[1 - \frac{\epsilon_\infty}{\epsilon_o}\right]. \quad (35)$$

Recent calculations [18] based on (14), (27), and (32)–(34) including the interference effect lead to the following corrected expression β_P^{dfi} in replacement to the above expression of β_P^{df} :

$$\beta_P^{\text{dfi}} = \left(\frac{2}{3f^3}\right) \alpha_C^2 \left(\frac{R_w}{R_g}\right)^3 \left(\frac{L_B}{b_S}\right) \left(\frac{L_S}{C_{\text{AP}}'}\right) \times \left[1 - \frac{\epsilon_\infty}{\epsilon_o}\right] \left| \left(f^3 - 4.808\right) + \frac{6.58}{|Z_S|} \right|, \quad (36)$$

$$f = \frac{b_S}{R_g}.$$

Notice that (35) and (36) are valid only in the case of slowly moving polyions so that $v_p \tau \leq R_g$. The evaluation of the interference effect in terms of the “interference parameter” $f = b_S/R_g \geq 2$ is quantified by the ratio between β_P^{dfi} in presence of interference and β_P^{df} in absence of interference:

$$\frac{\beta_P^{\text{dfi}}}{\beta_P^{\text{df}}} = \left| \left(1 - \frac{4.808}{f^3}\right) + \frac{6.58}{f^3 |Z_S|} \right| \leq 1, \quad f \geq 2. \quad (37)$$

This equation shows that for a discontinuous charge distribution, that is, $b_S \gg R_g$ ($f \gg 2$), the interference effect

becomes negligible. In contrast, it is maximal for a chain of tangent spheres ($f = 2$) and increases with $|Z_S|$.

It is interesting to note that β_P^{dfi} increases with dilution as α_C^2 and it reaches its maximal value β_P^{dfi} at infinite dilution, that is, when $\alpha_C = 1$ (Ostwald) and $C_{\text{AP}}' = \langle R_p \rangle$:

$$\beta_P^{\text{dfi}} = \left(\frac{2}{3}\right) \left(\frac{R_w}{b_S}\right)^3 \left(\frac{L_B}{b_S}\right) \left(\frac{L_S}{\langle R_p \rangle}\right) \left[1 - \frac{\epsilon_\infty}{\epsilon_o}\right] \times \left| \left(f^3 - 4.808\right) + \frac{6.58}{|Z_S|} \right|. \quad (38)$$

Finally it is important to underline the singular case of Manning's polyions ($R_g \cong 0$ and $L_S \rightarrow \infty$, $|Z_S| \rightarrow \infty$). Because of the infinite length of its moving chain, the structural state of the polyion (distribution of charges, distribution of solvent molecules, and therefore $\mathbf{P}(\mathbf{r}, t)$) varies periodically with time with a period equal to: $\theta = b_S/v_p$. As for slowly moving polyions, $v_p \tau \approx b_S$, therefore $\theta \approx \tau$, that is, the solvent molecules have not sufficient time to reorient themselves toward the new field $\mathbf{D}(\mathbf{r}, t)$ during the periodic variation. Consequently, the polyion seems to be immobile ($v_p = 0$) and thus surrounded by its initial symmetrical cylindrical distribution of solvent molecules. This conservation of the equilibrium symmetry implies the absence of any resulting dielectric relaxation field ($\Delta \mathbf{X}^{\text{df}} = 0$). It is the reason for which the dielectric relaxation effect is completely absent in the restrictive case of the Manning's model.

3. Results and Discussion

In order to emphasize the importance of the dielectric friction on stretched polyions at high dilution we studied the conductivity behaviors of the following polyelectrolytes: sodium heparinate of high molecular weight (RB21055), sodium chondroitin sulfate, and sodium polystyrene sulphonate (NaPSS). Details of the experimental protocols of conductivity measurements are given in previous papers [9–11]. Notice that conductivity results concerning (NaPSS) are those published by Vink [14]. Comparisons for each polyelectrolyte, between experimental equivalent conductivities $\Lambda_{\text{Poly}}^{\text{exp}} = 1000\chi/C_{\text{Na}^+}^{\text{e}}$ and theoretical equivalent conductivities $\Lambda_{\text{Poly}}^{\text{th}} = \alpha_C(\lambda_p + \lambda_i)$ calculated in absence or in presence of dielectric friction and also in absence or in presence of interference effect, are given in Tables 1–3 and Figures 2, 3, and 4. In each table we show the different molar total concentrations $C_{\text{Na}^+}^{\text{e}}$ of Na^+ counterions, the experimental equivalent conductivities $\Lambda_{\text{Poly}}^{\text{exp}}$ in $\text{cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$, the degrees of Na^+ condensation $(1 - \alpha_C)$ on polyions, the apparent charge numbers $Z_{\text{ap}} = \alpha_C Z_S$ of the polyions, the theoretical equivalent conductivities $\Lambda_{\text{Hy,El,R}}$ in absence of dielectric friction (i.e., only: hydrodynamic, electrophoretic, and ionic relaxation effects), the group radius R_g , the theoretical equivalent conductivities Λ_{Poly} in absence of interference, the theoretical equivalent conductivities Λ_{Poly}^i in presence of interference, the % of the dielectric friction effect β^{dfi} (36) in presence of interference,

and the ratios $\beta_p^{\text{dfi}}/\beta_p^{\text{df}}$ (37) expressing the relative importance of the interference effect (β_p^{df} is the dielectric friction effect in absence of interference).

3.1. Conductivity of Sodium Heparinate (RB21055). The biological polyelectrolyte sodium heparinate (RB21055) is a linear polysaccharide, well known for its anticoagulant activity. Its monomer unity is a hexasaccharide, in which each disaccharide consists in a glucosamine followed by an uronic acid. The charged groups are SO_3^- (NSO_3^- or OSO_3^-) and COO^- with a ratio $\text{OSO}_3^-/\text{COO}^- \approx 7/3$. This heparin is provided by Sigma as a sodium salt extracted from pork stomach. The physical characteristics of the Sodium heparinate (RB21055) are as follows:

$M_w \approx 10\,000 \text{ g}\cdot\text{mol}^{-1}$ is the average molecular weight of the Sodium Heparinate (RB21055).

$Z_S = -53 \pm 2$ at $\text{pH} \approx 7$ is the structural charge number.

$L_S = 160 \pm 8 \text{ \AA}$ is the structural length.

$b_S = 3.2 \pm 0.2 \text{ \AA}$ is the charge-to-charge distance.

$R_C = 10 \pm 1 \text{ \AA}$ is the cylindrical radius of the polyion chain.

Table 1 shows that the variation of the degree of dissociation α_C of Na^+ from heparin in the concentration range: $5 \times 10^{-5} \text{ M} < \text{C}_{\text{Na}^+} < 5 \times 10^{-3} \text{ M}$ is in conformity with the dilution principle so that α_C increases with dilution from 0.59 to 0.76 and it differs from its Manning's value $\alpha_M = b_S/|Z_i|L_B = 0.44$. Consequently, the apparent charge number $Z_{\text{ap}} = \alpha_C Z_S$ varies with the concentration from -37.8 for $\text{C}_{\text{Na}^+} = 5.11 \times 10^{-5} \text{ M}$ to -29.5 for $\text{C}_{\text{Na}^+} = 5.13 \times 10^{-3} \text{ M}$. Notice that this last value seems to be different from the value $Z_{\text{ap}} = -18$ obtained from electrophoretic mobility using Nernst-Einstein relation: $u_p/D_p = |Z_{\text{ap}}|e/k_B T$ with $D_p \approx 7 \times 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$ [22]. In fact Z'_{ap} differs from Z_{ap} because it depends at the same time on ionic condensation (α_C) and on ionic friction effects via u_p . Table 1 and Figure 2 show that the experimental conductivity $\Lambda_{\text{NaHRB}}^{\text{exp}}$ of sodium heparinate (RB21055) decreases sharply from 82.6 to $61.9 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$ in the low concentration range: $5 \times 10^{-5} \text{ M} < \text{C}_{\text{Na}^+} < 5 \times 10^{-4} \text{ M}$. Theoretically, the hydrodynamic contribution (at infinite dilution) $\Lambda_{\text{NaHRB}}^{\text{HD}}$ to $\Lambda_{\text{NaHRB}}^{\text{exp}}$ is obtained in absence of ionic condensation ($\alpha_C = 1$), of ionic frictions ($\Delta\lambda_p^{\text{cl}} = 0$, $\beta_p^{\text{ir}} = 0$) and in absence of dielectric friction ($\beta_p^{\text{df}} = 0$). According to (6), (10), (16), and (17), $\Lambda_{\text{NaHRB}}^{\text{HD}} = (\lambda_{\text{HRB}}^{\text{HD}} + \lambda_{\text{Na}^+}^{\text{HD}})$ with $\lambda_{\text{Na}^+}^{\text{HD}} = 50.1$, $\lambda_{\text{HRB}}^{\text{HD}} = |Z_S|Fe/6\pi\eta\langle R_p \rangle$. The mean radius $\langle R_p \rangle$ of heparinate (RB21055) is calculated from (10). We found $\langle R_p \rangle = 28.8 \text{ \AA}$, $\lambda_{\text{HRB}}^{\text{HD}} = 159.84$, and $\Lambda_{\text{NaHRB}}^{\text{HD}} = 210 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$. Table 1 shows that the dielectric friction ($\beta_p^{\text{dfi}} > 50\%$) is the most significant retarding effect by comparison to the electrophoretic effect and the ionic relaxation effect even when taking into account the interference of the local displacement fields. Now, as β_p^{dfi} is proportional to $(\alpha_C)^2$

then $\beta_p^{\text{dfi}} \approx (\alpha_C)^2 \beta_p^{\text{odfi}}$, which means that β_p^{dfi} increases with dilution toward its maximal value β_p^{odfi} at infinite dilution ($\alpha_C = 1$). According to (38), β_p^{odfi} depends on the interference factor $f = b_S/R_g$. Adjustment between experimental conductivities $\Lambda_{\text{NaHRB}}^{\text{exp}}$ and theoretical conductivities Λ_{NaHRB}^i of heparinate (RB21055) leads to a group radius equal to $R_g = 1.65 \pm 0.05 \text{ \AA}$ so that $f \approx 2$ (a succession of tangent charged spheres). The maximal value β_p^{odfi} is therefore equal to $\beta_p^{\text{odfi}} = (2/3)(R_w/b_S)^3(L_B/b_S)(L_S/\langle R_p \rangle)[1 - \epsilon_{\infty}/\epsilon_0](f^3 - 4.808) + 6.58/|Z_S| = 2.25$, for $b_S = 3.2 \text{ \AA}$, $f \approx 2$, $L_S = 160 \text{ \AA}$ and $R_w = 1.4 \text{ \AA}$. Consequently, the correct limiting conductivity at infinite dilution $\Lambda_{\text{NaHRB}}^{\circ}$ must take into account the limiting dielectric friction effect β_p^{odfi} in addition to the hydrodynamic friction as follows: $\Lambda_{\text{NaHRB}}^{\circ} = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{HRB}}^{\circ\text{HD}}/(1 + \beta_p^{\text{odfi}}) = 50.1 + 49.2 = 99.3 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$. This $\Lambda_{\text{NaHRB}}^{\circ}$ is experimentally inaccessible because of the nonexistence of a universal limiting law allowing a rigorous extrapolation of $\Lambda_{\text{HRB}}^{\text{exp}}$ at infinite dilution. This impossibility is due primarily to ionic condensation effect. However, according to (6), (7), and (11), and after neglecting ionic friction effects, we can derive the following approximate complex relation between $\Lambda_{\text{NaHRB}}^{\text{exp}}$ and α_C applicable in the range of very dilute solutions for which the stretched conformation is favored and for which the electrophoretic effects and ionic relaxation effects are negligible:

$$\begin{aligned} \Lambda_{\text{NaHRB}}^{\text{exp}} &\approx \alpha_C \left[\lambda_{\text{Na}^+}^{\circ} + \frac{\alpha_C \lambda_{\text{HRB}}^{\circ\text{HD}}}{(1 + \alpha_C^2 \beta_p^{\text{odfi}})} \right] \\ &\approx \alpha_C \left[50.1 + \frac{159.84 \alpha_C}{(1 + 2.25 \alpha_C^2)} \right]. \end{aligned} \quad (39)$$

This expression can be used as an indirect method to evaluate experimentally the degree of ionic condensation $(1 - \alpha_C)$ from experimental measurements of the equivalent conductivity of the polyelectrolyte at high dilution. Calculation shows that for $\text{C}_{\text{Na}^+} < 10^{-4} \text{ M}$, $\alpha_C \geq 0.8$ in conformity with theoretical values ((1)–(4)) but incompatible with the Manning's value $\alpha_M = b_S/L_B \approx 0.44$. It is important to notice at this stage that the constancy of the condensation parameter at high dilution with $\alpha_C = \alpha_M$ would imply that $\Lambda_{\text{NaHRB}}^{\text{exp}}$ increases first with dilution then attains a “palier” (platform) in the range of very low concentrations in which α_C obeys to the Manning's model. This kind of behavior is not in general experimentally observed [14].

In order to reinforce the hypothesis of the stretched conformation at high dilution we will compare the equivalent conductivity of sodium heparinate $\Lambda_{\text{NaHRB}}^{\text{sph}}$ calculated in the case of coiled conformation (quasi-spherical) having a mean radius $R_S \approx \langle R_p \rangle \approx k_B T/6\pi\eta D_p \approx 30 \text{ \AA}$, to its corresponding experimental equivalent conductivity $\Lambda_{\text{NaHRB}}^{\text{exp}}$. According to Zwanzig-Frank notation [19, 25] the expression of the equivalent conductivity $\lambda_{\text{HRB}}^{\text{sph}}$ of the spherical polyion at very high dilution is $\lambda_{\text{HRB}}^{\text{sph}} \approx A \alpha_{\text{sph}} |Z_S|/[R_S + (\alpha_{\text{sph}}^2 Z_S^2 C/R_S^3)]$, with $A = 92$, $C = 10$ at 25°C in water, $R_S = 30 \text{ \AA}$, and $|Z_S| = 53$. The equivalent conductivity of the (spherical)

TABLE 1: Variations with counterions concentration $C_{Na^+}^{exp}$ of the experimental Λ_{NaHRB}^{exp} and theoretical Λ_{NaHRB}^i equivalent conductivities, of the degree of Na^+ condensation $(1 - \alpha_C)$, of the apparent charge number Z_{ap} , and of the dielectric frictions in absence (β^{df}) and in presence (β^{dfi}) of interference, in the case of sodium heparinate RB21055 in water at 25°C.

$C_{Na^+}^{exp}$ mol·L ⁻¹	Λ_{NaHRB}^{exp} $cm^2 \cdot \Omega^{-1} \cdot eqV_{Na^+}^{-1}$	$1 - \alpha_C$	Z_{ap}	Λ_{NaHRB}^{exp} $cm^2 \cdot \Omega^{-1} \cdot eqV_{Na^+}^{-1}$	Λ_{NaHRB}^i $cm^2 \cdot \Omega^{-1} \cdot eqV_{Na^+}^{-1}$	R_g (Å)	Λ_{NaHRB}^i $cm^2 \cdot \Omega^{-1} \cdot eqV_{Na^+}^{-1}$	$100\beta^{dfi}$	$\beta_P^{dfi}/\beta_P^{df}$
5.1083×10^{-5}	82.61	0.244	-37.80	117.58	59.62	1.691	82.68	78.03	0.30
7.4666×10^{-5}	80.73	0.262	-36.91	111.18	58.19	1.70	80.67	70.03	0.30
1.4152×10^{-4}	74.72	0.291	-35.45	100.68	55.06	1.693	74.73	66.14	0.30
2.4088×10^{-4}	69.51	0.314	-34.29	92.31	52.18	1.678	69.15	66.08	0.32
5.0027×10^{-4}	61.87	0.344	-32.82	81.54	48.29	1.656	61.96	65.73	0.35
9.3208×10^{-4}	56.72	0.366	-31.72	73.27	45.29	1.643	56.79	62.98	0.36
1.7299×10^{-3}	52.04	0.385	-30.77	66.05	42.51	1.627	52.08	60.87	0.37
3.3723×10^{-3}	48.29	0.402	-29.94	59.47	40.16	1.623	48.26	54.60	0.38
5.1303×10^{-3}	46.34	0.410	-29.55	55.92	38.95	1.625	46.31	49.80	0.38

FIGURE 2: Comparison between variations with $C_{Na^+}^o$ of experimental (Λ_{NaHRB}^{exp} , blue $\diamond$ points) and theoretical equivalent conductivities ($\Lambda_{Hy,El,R}$ without dielectric friction, Λ_{NaHRB} with dielectric friction in absence of interference, Λ_{NaHRB}^i with dielectric friction in presence of interference) of sodium heparinate RB21055 in water at 25°C.

sodium heparinate is therefore $\Lambda_{NaHRB}^{Sph} \approx \alpha_{Sph}(\lambda_{Na^+}^{Sph} + \lambda_{HRB}^{Sph})$. Now, according to the ionic association theory of Fuoss [3] the degree of dissociation: $\alpha_{Sph} > 0.68$ for $C_{Na^+}^o < 10^{-4}$ M, therefore $\Lambda_{NaHRB}^{Sph} > 100 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{Na^+}^{-1}$. This expected result is at least twenty percent larger (20%) than the experimental equivalent conductivity Λ_{NaHRB}^{exp} ($\sim 83 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{Na^+}^{-1}$), and it therefore invalidates the hypothesis of spherical conformation for heparin RB21055 polyions at high dilution. Finally it is important to underline the following principal conclusions.

- (i) The interference effect decreases by 70%–60% the dielectric friction on the stretched polyion. However, despite this important attenuation, the resulting dielectric friction remains the principal frictional effect (β_p^{dfi} decreases with concentration from 78% to 50%) in comparison to ionic relaxation effect and electrophoretic effect.
- (ii) The adjustment of the experimental equivalent conductivities Λ_{NaHRB}^{exp} with the theoretical conductivities Λ_{HRB}^i leads to a group radius R_g sensibly constant, of about $1.65 \pm 0.05 \text{ \AA}$, that is, equal to the half of the distance $b_s = 3.2 \pm 0.2 \text{ \AA}$ between two successive spherical charged groups, so that the coherent condition: $f = b_s/R_g = \text{constant} \geq 2$ is verified in the studied concentration range.
- (iii) The ionic relaxation effect β^{ir} on polyions and counterions becomes important (10%–20%) for $C_{Na^+}^o > 10^{-4}$ M, while β^{ir} is $< 6\%$ for highly dilute solutions. This result is not in conformity with the Manning prediction: $\beta^{ir} \rightarrow 13\%$.
- (iv) The electrophoretic effect is relatively weak for Na^+ counterions ($< 6\%$), while it decreases as expected with dilution from 28% to 4% in the case of stretched heparin polyions.

- (v) The degree of ionic condensation ($1 - \alpha_C$) of Na^+ on heparin RB21055 increases in % with the concentration from 24% to 41% and differs from the Manning value: 56%.
- (vi) The sharp increasing with dilution of the equivalent conductivity of sodium heparinate proves that both thermodynamics behavior and electrolytic conductivity behavior of this polyelectrolyte are governed by the Ostwald concentration regime despite the stretched conformation of heparin polyions.

3.2. Conductivity of Sodium Chondroitin Sulfate. The biological polyion chondroitin sulfate is a large linear polysaccharide composed of repeating disaccharide units altering an amino sugar *N*-acetyl- β -galactosamine-4-sulfate and an β -glucuronic acid. The sulfate groups as well as the uronic acids result in linear chains having a negative charge. Chondroitin sulfate is provided by Sigma as a sodium salt from bovine trachea. The physical characteristics of the macroion are [10, 11] as follows:

$M_W \approx 21430 \text{ g} \cdot \text{mol}^{-1}$ is the average molecular weight of the used polyelectrolyte.

$Z_S = -75 \pm 3$ is the structural charge number.

$L_S = 435 \pm 15 \text{ \AA}$ is the structural length.

$b_s = 5.8 \pm 0.2 \text{ \AA}$ is the charge-to-charge distance.

$R_C = 6 \pm 0.5 \text{ \AA}$ is the cylindrical radius of the polyion chain.

This polyion is therefore about three times longer than heparin RB, and regarding its significant charge separation b_s , it presents a more discontinuous linear charge distribution. On the other hand, according to Manning's theory, we expect a weaker degree of condensation ($1 - \alpha_C$) despite the relative importance of its structural charge number. Table 2 shows that the degree of dissociation α_C of Na^+ from chondroitin increases slightly with dilution from 0.804 to 0.852 in the concentration range: $1.38 \times 10^{-4} \text{ M} < C_{Na^+}^o < 1.11 \times 10^{-3} \text{ M}$. Sodium chondroitin sulfate is one of peculiar polyelectrolytes for which the behavior of ionic condensation in aqueous solution is compatible at the same time with the model of Manning and with the principle of dilution [10, 11]. Indeed, the Manning's value of the condensation parameter is $\alpha_M = b_s/|Z_i|L_B = 0.81$. Consequently, the apparent charge number $Z_{ap} = \alpha_C Z_S$ varies slightly with the concentration from -63.9 for $C_{Na^+}^o = 1.38 \times 10^{-4} \text{ M}$ to -60.3 for $C_{Na^+}^o = 1.11 \times 10^{-3} \text{ M}$.

Table 2 and Figure 3 show that the experimental conductivity of sodium chondroitin $\Lambda_{NaChondro}^{exp}$ increases with dilution in a monotonous way from 65.3 to $78.54 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{Na^+}^{-1}$ in the concentration range: $1.38 \times 10^{-4} \text{ M} < C_{Na^+}^o < 1.11 \times 10^{-3} \text{ M}$, (i.e., without the appearance of any palier). The hydrodynamic contribution (at infinite dilution) $\Lambda_{NaChondro}^{oHD}$ to $\Lambda_{NaChondro}^{exp}$ is obtained in absence of ionic condensation and in absence of other frictional effects from

TABLE 2: Variations with counterions concentration $C_{Na^+}^o$ of the experimental $\Lambda_{NaChond}^{exp}$ and theoretical $\Lambda_{NaChond}^i$ and $\Lambda_{NaChond}^{df}$ equivalent conductivities, of the degree of Na^+ condensation ($1 - \alpha_C$), of the apparent charge number Z_{ap} , and of the dielectric frictions in absence ($\beta_{Na^+}^{df}$) and in presence ($\beta_{Na^+}^{dfi}$) of interference, in the case of sodium chondroitin sulfate in water at 25 °C.

$C_{Na^+}^o$ mol·L ⁻¹	$\Lambda_{NaChond}^{exp}$ cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	$1 - \alpha_C$	Z_{ap}	Λ_{HylR}^{exp} cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	R_g (Å)	$\Lambda_{NaChond}^i$ cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	$\Lambda_{NaChond}^{df}$ cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	$100\beta_{Na^+}^{dfi}$	$\beta_{Na^+}^{df}/\beta_{Na^+}^{dfi}$
1.3868×10^{-4}	78.54	0.148	-63.93	112.76	2.15	73.47	78.69	92.3	0.76
1.5944×10^{-4}	77.93	0.152	-63.62	110.80	2.15	72.75	77.85	90.6	0.76
1.7674×10^{-4}	76.99	0.155	-63.40	109.38	2.14	71.97	76.91	91.1	0.76
2.1070×10^{-4}	75.74	0.160	-63.03	107.04	2.14	71.11	75.91	88.9	0.76
2.6553×10^{-4}	74.02	0.166	-62.57	104.11	2.12	69.55	74.04	89.4	0.77
3.1443×10^{-4}	73.16	0.171	-62.24	102.09	2.12	68.82	73.19	87.3	0.77
3.2445×10^{-4}	72.86	0.172	-62.19	101.72	2.11	68.45	72.74	88.5	0.77
4.0603×10^{-4}	71.42	0.176	-61.79	99.20	2.11	67.55	71.69	85.7	0.77
4.4241×10^{-4}	70.85	0.178	-61.65	98.29	2.09	66.77	70.73	87.8	0.77
5.0362×10^{-4}	69.92	0.181	-61.43	96.62	2.08	66.08	69.90	87.7	0.78
5.1437×10^{-4}	69.95	0.182	-61.40	96.71	2.08	66.00	69.81	87.4	0.78
5.1480×10^{-4}	70.06	0.182	-61.40	96.70	2.09	66.23	70.09	85.8	0.78
6.7844×10^{-4}	68.38	0.187	-60.98	93.97	2.08	65.07	68.72	83.8	0.78
6.9613×10^{-4}	67.94	0.188	-60.94	93.72	2.08	64.77	68.35	85.1	0.78
1.0479×10^{-3}	65.88	0.195	-60.39	89.96	2.05	63.11	66.36	82.8	0.79
1.1149×10^{-3}	65.29	0.196	-60.31	89.41	2.02	62.31	65.39	86.6	0.80

FIGURE 3: Comparison between variations with C_{Na^+} of experimental ($\Lambda_{NaChondro}^{exp}$, blue $\diamond$ points) and theoretical equivalent conductivities ($\Lambda_{Hy,El,R}$ without dielectric friction, $\Lambda_{NaChondro}$ with dielectric friction in absence of interference, $\Lambda_{NaChondro}^i$ with dielectric friction in presence of interference) of sodium chondroitin sulfate in water at 25°C.

(6), (10), (16), and (17), so that $\Lambda_{NaChondro}^{\circ HD} = (\lambda_{Na^+}^{\circ HD} + \lambda_{Na^+}^{\circ})$ with $\lambda_{Na^+}^{\circ} = 50.1$ with $\lambda_{Na^+}^{\circ HD} = |Z_S|Fe/6\pi\eta\langle R_p \rangle$. The mean radius $\langle R_p \rangle$ of the chondroitin sulfate is equal to 50.8 Å, therefore $\lambda_{Na^+}^{\circ HD} = 136.1$ and $\Lambda_{NaChondro}^{\circ HD} = 186.2 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqvNa}^+^{-1}$. Table 2 shows also that the dielectric friction ($\beta_P^{dfi} > 85\%$) is the most significant retarding effect by comparison to the electrophoretic effect and the ionic relaxation effect even when taking into account the interference of the local displacement fields. β_P^{dfi} depends on the interference factor $f = b_S/R_g$. Adjustment between experimental and theoretical conductivities of chondroitin sulfate leads to a group radius equal to $R_g = 2.14 \pm 0.2 \text{ Å}$ so that $f = b_S/R_g = 2.71$ (a discontinuous linear charge distribution), the maximal value β_P^{dfi} is, according to (38), equal to $\beta_P^{dfi} = (2/3)(R_w/b_S)^3(L_B/b_S)(L_S/\langle R_p \rangle)[1 - \epsilon_{\infty}/\epsilon_0][(f^3 - 4.808) + 6.58/|Z_S|] = 1.47$ for $b_S = 5.8 \text{ Å}$, $f \approx 2.7$, $L_S = 435 \text{ Å}$ and $R_w = 1.4 \text{ Å}$. Consequently, the new limiting $\Lambda_{NaChondro}^{\circ}$ must take into account the limiting dielectric friction effect β_P^{dfi} in addition to the hydrodynamic friction as follows: $\Lambda_{NaChondro}^{\circ} = \lambda_{Na^+}^{\circ} + \lambda_{Na^+}^{\circ HD}/(1 + \beta_P^{dfi}) = 50.1 + 36.7 = 86.8 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqvNa}^+^{-1}$. This $\Lambda_{NaChondro}^{\circ}$ is experimentally inaccessible. However, according to our previous analysis and to (6), (7), and (11), we can proceed in the same manner that for Heparin RB21055 in order to derive the following approximate relation between the experimental equivalent conductivity of chondroitin sulfate $\Lambda_{NaChondro}^{exp}$ and the degree of dissociation α_C in the range of very dilute solutions for which the stretched conformation is favored and for which the electrophoretic effects and ionic relaxation effects are negligible, we obtain

$$\begin{aligned} \Lambda_{NaChondro}^{exp} &\approx \alpha_C \left[\lambda_{Na^+}^{\circ} + \frac{\alpha_C \lambda_{Na^+}^{\circ HD}}{(1 + \alpha_C^2 \beta_P^{dfi})} \right] \\ &\approx \alpha_C \left[50.1 + \frac{136.13 \alpha_C}{(1 + 1.47 \alpha_C^2)} \right]. \end{aligned} \quad (40)$$

In conclusion we can underline the following points.

- (i) The interference effect decreases by 25% the dielectric friction on stretched chondroitin sulfate polyions. However, despite this attenuation, the resulting dielectric friction remains the principal frictional effect (β_P^{dfi} decreases with concentration from 92% to 86%) in comparison to ionic relaxation effect and electrophoretic effect.
- (ii) The adjustment of experimental equivalent conductivities $\Lambda_{NaChondro}^{exp}$ with the theoretical conductivities $\Lambda_{NaChondro}^i$ leads to a group radius R_g sensibly constant of about $2.13 \pm 0.2 \text{ Å}$ so that the coherent condition: $f = b_S/R_g = 2.7 \geq 2$ is verified in the studied concentration range.
- (iii) The ionic relaxation effect β^{ir} on chondroitin polyions and Na^+ counterions remains approximately constant ($\sim 15\%$) in the studied range of relatively low concentrations: $1.38 \times 10^{-4} \text{ M} < C_{Na^+} < 1.11 \times 10^{-3} \text{ M}$ in conformity with the Manning prediction.
- (iv) The electrophoretic effect is relatively weak for the Na^+ counterions ($< 4\%$), while it normally decreases with dilution from 27% to 12% for stretched chondroitin sulfate polyions.
- (v) The degree of ionic condensation $(1 - \alpha_C)$ of Na^+ on stretched chondroitin sulfate polyions increases in % slowly with the concentration from 15% to 19.6%. These values are close to the Manning value: $(1 - \alpha_M) = 0.19$.
- (vi) The weak increasing with dilution of the equivalent conductivity of sodium chondroitin sulfate proves that both thermodynamics behavior and electrolytic conductivity behavior of this polyelectrolyte at very high dilution are intermediate between the Ostwald concentration regime and the Manning concentration regime.

3.3. Conductivity of Sodium Polystyrene Sulphonate (NaPSS). Polystyrene sulphonate is a linear chain of 4-styrenesulfonic acid groups. The linear formula of NaPSS is $-(C_8H_7NaO_3S)_n-$; it is provided by Aldrich Chemicals as a sodium salt. The physical characteristics of the studied sodium polystyrene sulphonate are as follows:

$M_W \approx 600000$ is the average molecular weight in $\text{g}\cdot\text{mol}^{-1}$ of the used polyelectrolyte. $Z_S = -2900 \pm 120$ is the structural charge number.

$L_S = 7250 \pm 300 \text{ \AA}$ is the structural length.

$b_S = 2.5 \pm 0.1 \text{ \AA}$ is the charge-to-charge distance.

$R_C = 6.9 \pm 0.5 \text{ \AA}$ is the cylindrical radius of the polyion chain.

Table 3 shows that the degree of dissociation α_C of Na^+ from PSS decreases very slightly with dilution from 0.441 to 0.457 in the concentration range: $1.16 \times 10^{-3} \text{ M} < C_{\text{Na}^+} < 5.14 \times 10^{-3} \text{ M}$. This behavior seems in contradiction with the Ostwald regime. However this slight variation is not very significant in regard of uncertainties and we can assume that α_C remains sensibly constant. In fact, theoretical formal calculations according to (1) show that α_C presents a little minimum (0.413) for $C_{\text{Na}^+} \approx 10^{-5} \text{ M}$, then it increases slowly according to the principle of dilution until 0.605. We can therefore distinguish between two concentration ranges or regimes: (a) the Manning regime: $1 \times 10^{-5} \text{ M} < C_{\text{Na}^+} < 5.1 \times 10^{-3} \text{ M}$, in which α_C remains practically constant, and (b) a formal Ostwald concentration regime: $C_{\text{Na}^+} \ll 1 \times 10^{-5} \text{ M}$, in which α_C increases with dilution. Because of the large length of PSS (7250 $\text{\AA}$) it is not possible to experimentally observe highly diluted regime via the increasing of conductivity. Only the Manning concentration regime was experimentally observed via the constancy of the equivalent conductivity of NaPSS during dilution in the studied concentration range. Note that the Manning regime has also been observed for NaPSS polyelectrolytes of molar masses M_w between $8000 \text{ g}\cdot\text{mol}^{-1}$ and $360000 \text{ g}\cdot\text{mol}^{-1}$ [16]. However, despite the large length of PSS and despite the constancy of its degree of dissociation, the actual value ~ 0.45 of α_C is in fact different from its Manning's value $\alpha_M = b_S/|Z_i|L_B = 0.35$. Consequently, the apparent charge number Z_{ap} varies with the concentration from -1326 for $C_{\text{Na}^+} = 5.14 \times 10^{-3} \text{ M}$ to -1279 for $C_{\text{Na}^+} = 1.16 \times 10^{-3} \text{ M}$.

Table 3 and Figure 4 show that the experimental conductivity $\Lambda_{\text{NaPSS}}^{\text{exp}}$ decreases very slowly with concentration in a monotonous way from 35.5 to $34.9 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$ in the indicated concentration range. The mean radius $\langle R_p \rangle$ of the polyion is equal to $521.2 \text{ \AA}$; therefore according to (16)–(18) the hydrodynamic mobility $\lambda_{\text{PSS}}^{\text{HD}}$ of the PSS polyion is equal to $\lambda_{\text{PSS}}^{\text{HD}} = |Z_S|/6\pi\eta\langle R_p \rangle = 512.8 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$. Adjustment between experimental and theoretical conductivities of NaPSS polyelectrolyte leads to a constant group radius equal to $R_g \cong 1.21 \text{ \AA}$ so that $f = b_S/R_g = 2.06$ (a quasi-continuous linear charge distribution of tangent spheres); the maximal value of β_p^{dfi} is therefore $\beta_p^{\text{dfi}} = (2/3)(R_w/b_S)^3(L_B/b_S)(L_S/\langle R_p \rangle)[1 - \epsilon_{\infty}/\epsilon_o]((f^3 - 4.808) + 6.58/|Z_S|) = 17.9$ for $b_S = 2.5 \text{ \AA}$, $f \approx 2$, $L_S = 7250 \text{ \AA}$

FIGURE 4: Comparison between variations with C_{Na^+} of experimental ($\Lambda_{\text{NaPSS}}^{\text{exp}}$, blue $\diamond$ points) and theoretical equivalent conductivities ($\Lambda_{\text{Hy,EL,R}}$ without dielectric friction, Λ_{NaPSS} with dielectric friction in absence of interference, Λ_{NaPSS}^i with dielectric friction in presence of interference) of sodium polystyrene sulphonate in water at 25°C .

and $R_w = 1.4 \text{ \AA}$. Using our previous analysis and (6), (7), and (11), we can proceed in the same manner that for Heparin and Chondroitin in order to derive the following approximate relation between $\Lambda_{\text{NaPSS}}^{\text{exp}}$ and α_C , in the range of dilute solutions for which the stretched conformation is favored, we obtain

$$\Lambda_{\text{NaPSS}}^{\text{exp}} \approx \alpha_C \left[\frac{\lambda_{\text{Na}^+}^{\text{exp}} + \alpha_C \lambda_{\text{PSS}}^{\text{HD}}}{(1 + \alpha_C^2 \beta_p^{\text{dfi}})} \right] \approx \alpha_C \left[\frac{50.1 + 512.8 \alpha_C}{(1 + 17.9 \alpha_C^2)} \right]. \quad (41)$$

Now, as α_C undergoes weak variation in the Manning region, $\Lambda_{\text{NaPSS}}^{\text{exp}}$ remains sensibly constant (palier of $\Lambda_{\text{NaPSS}}^{\text{exp}} \sim 35 \text{ cm}^2 \cdot \Omega^{-1} \cdot \text{eqv}_{\text{Na}^+}^{-1}$), in the concentration range: $1 \times 10^{-3} \text{ M} < C_{\text{Na}^+} < 5 \times 10^{-3} \text{ M}$. We can however formally expect the emergence of highly diluted regime for $C_{\text{Na}^+} < 10^{-6} \text{ M}$. It is also important to underline that the experimental observation of Manning behavior proves the veracity of the stretched conformation. Indeed, it is well known that for spherical conformation the degree of dissociation α_S increases normally with dilution (Fuoss behavior) so that we will not be able to observe in this case any palier of conductivity.

In conclusion we can underline the following points.

- (i) The interference effect decreases by 55% the dielectric friction on PSS polyions. However, despite this attenuation, and particularly in this case of very long chains, the dielectric friction remains the principal frictional effect (β_p^{dfi} decreases with concentration from 172% to 142%) in comparison to ionic relaxation effect and electrophoretic effect.
- (ii) The adjustment of experimental equivalent conductivities $\Lambda_{\text{NaPSS}}^{\text{exp}}$ with the theoretical conductivities Λ_{NaPSS}^i leads to a group radius R_g sensibly constant of about $1.21 \text{ \AA}$ so that the coherent condition:

TABLE 3: Variations with counterions concentration $C_{Na^+}^o$ of the experimental Λ_{NaPSS}^{exp} and theoretical Λ_{NaPSS} and Λ_{NaPSS}^i equivalent conductivities, of the degree of Na^+ condensation $(1 - \alpha_C)$, of the apparent charge number Z_{ap} , and of the dielectric frictions in absence (β^{df}) and in presence (β^{dfi}) of interference, in the case of sodium polystyrene sulphonate in water at 25°C. Distinction between Manning concentration regime and *Ostwald* concentration regime.

$C_{Na^+}^o$ mol·L ⁻¹	Λ_{NaPSS}^{exp} cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	$1 - \alpha_C$	Z_{ap}	Λ_{HVELR} cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	R_g (Å)	Λ_{NaPSS} cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	Λ_{NaPSS}^i cm ² · Ω ⁻¹ · eqv _{Na⁺} ⁻¹	$100\beta^{dfi}$	$\beta_P^{dfi} / \beta_P^{df}$
1×10^{-10}		0.395	-1754	216.9	1.21	42.13	54.55	698	0.45
1×10^{-9}		0.447	-1605	182.4	1.21	39.21	51.16	558	0.45
1×10^{-8}		0.497	-1460	149.75	1.21	36.08	47.40	459	0.45
1×10^{-7}		0.543	-1328	118.56	1.21	32.55	43.03	373	0.45
1×10^{-6}		0.576	-1229	91.22	1.21	29.01	38.40	303	0.45
1×10^{-5}		0.587	-1196	78.03	1.21	28.03	36.65	252	0.45
1×10^{-4}		0.579	-1221	70.55	1.21	28.45	36.45	213	0.45
1.159×10^{-3}	35.52	0.559	-1279	60.98	1.21	28.52	35.53	172	0.45
2.151×10^{-3}	35.37	0.553	-1298	58.41	1.212	28.55	35.38	159	0.45
2.416×10^{-3}	35.33	0.551	-1302	57.92	1.212	28.55	35.33	157	0.45
3.526×10^{-3}	35.16	0.547	-1314	56.31	1.214	28.54	35.16	149	0.45
5.142×10^{-3}	34.88	0.543	-1326	54.64	1.214	28.49	34.88	142	0.45

$f = b_s/R_g = 2.06 \geq 2$ is verified in the studied concentration range.

- (iii) The ionic relaxation effect β^{ir} on PSS polyions and Na^+ counterions is relatively important and remains sensibly constant ($\sim 14\%$) in the studied range of relatively low concentrations: $1.16 \times 10^{-3} \text{ M} < \text{C}_{\text{Na}^+}^{\circ} < 5.14 \times 10^{-3} \text{ M}$. The reason of the constancy of the relaxation effect is the large chain length of PSS (7250 Å) by comparison to the minor axis of the ionic atmosphere d_p . Indeed, $d_p = 199 \text{ Å}$ for $\text{C}_{\text{Na}^+}^{\circ} = 1.16 \times 10^{-3} \text{ M}$ and $d_p = 98 \text{ Å}$ for $\text{C}_{\text{Na}^+}^{\circ} = 5.14 \times 10^{-3} \text{ M}$. Therefore, $d_p/L_S < 0.03$ and according to (23), $\beta_p^{\text{ir}} \approx (\alpha_C/\alpha_M)(1/9) \approx 0.14$ for all $\text{C}_{\text{Na}^+}^{\circ}$.
- (iv) The electrophoretic effect ($\Delta\lambda_p^{\text{el}}/\lambda_p^{\circ\text{HD}} = \langle R_p \rangle / \langle d_p \rangle$) on PSS polyions is more important than β^{ir} in the studied concentration range; it decreases slowly with dilution from 61.9% to 51.7%. The electrophoretic effect on PSS becomes formally negligible ($<5\%$) for highly dilute solution: $\text{C}_{\text{Na}^+}^{\circ} < 10^{-6} \text{ M}$.
- (v) The observed conductivity variation of NaPSS in the concentration range: $1.16 \times 10^{-3} \text{ M} < \text{C}_{\text{Na}^+}^{\circ} < 5.14 \times 10^{-3} \text{ M}$ reveals a behavior compatible with the Manning concentration regime because of the large length of its stretched chain.

4. Conclusions

In this work we have used electrolytic conductivity as a powerful tool to investigate, in dilute aqueous solutions at 25°C, the behavior of three kinds of flexible polyelectrolytes of different chain lengths L_S and different charge distances b_s and without added salt: sodium heparinate ($L_S = 160 \text{ Å}$, $b_s = 3.2 \text{ Å}$), sodium chondroitin sulfate ($L_S = 435 \text{ Å}$, $b_s = 5.8 \text{ Å}$), and sodium polystyrene sulphonate ($L_S = 7250 \text{ Å}$, $b_s = 2.5 \text{ Å}$). A strong influence on their equivalent conductivities Λ_{Poly} has been shown to exist due to the interdependent effects of Na^+ condensation and of dielectric friction and particularly when their chains adopt a stretched conformation at high dilute solutions. In contrast, the ionic friction effects on counterions and polyions due to the electrophoretic effects ($\Delta\lambda_{\text{Na}^+}^{\text{el}}$, $\Delta\lambda_p^{\text{el}}$) and to the ionic relaxation effect (β^{ir}) are less important and become negligible at high dilution. The correlation between Λ_{Poly} and, respectively, the degree of condensation ($1 - \alpha_C$), the limiting equivalent conductivity $\lambda_{\text{Na}^+}^{\circ}$, the hydrodynamic equivalent conductivity of the polyion $\lambda_p^{\circ\text{HD}}$, the limiting dielectric friction coefficient (β_p^{df}), and the ionic friction terms ($\Delta\lambda_{\text{Na}^+}^{\text{el}}$, $\Delta\lambda_p^{\text{el}}$, β^{ir}) can be expressed by the following general expression:

$$\Lambda_{\text{Poly}} \approx \alpha_C (1 + \beta^{\text{ir}})^{-1} \times \left[(\lambda_{\text{Na}^+}^{\circ} - \Delta\lambda_{\text{Na}^+}^{\text{el}}) + \frac{(\alpha_C \lambda_p^{\circ\text{HD}} - \Delta\lambda_p^{\text{el}})}{(1 + \alpha_C^2 \beta_p^{\text{df}})} \right] \quad (42)$$

The limiting dielectric friction coefficient (β_p^{df}) is very sensitive to the conformation of the polyion, to the charge distance b_s , and to the radius R_g of charged groups. Indeed, (β_p^{df}) is weak for coiled conformations and vanishes when $v_p \tau > R_g$, where v_p is the velocity of the polyion and τ is the dielectric relaxation time of the solvent molecules. In contrast, for a stretched chain of charged spheres, (β_p^{df}) is in general larger than 50% and increases with the interference term $f^3 = (b_s/R_g)^3$ as follows:

$$\beta_p^{\text{df}} = \left(\frac{2}{3}\right) \left(\frac{R_w}{b_s}\right)^3 \left(\frac{L_B}{b_s}\right) \left(\frac{L_S}{\langle R_p \rangle}\right) \left[1 - \frac{\epsilon_{\infty}}{\epsilon_0}\right] \times \left| (f^3 - 4.808) + \frac{6.58}{|Z_S|} \right| \sim \text{Ln} \left(\frac{L_S}{R_C} \right) \quad (43)$$

On the basis of our data and of our analysis, we can provisionally conclude that it is not possible to propose a universal model in order to describe the electrolytic conductivity behavior of polyelectrolytes having whichever chain lengths and distances between charged groups. However, two concentration regimes could be identified: (a) the Ostwald concentration regime (it is the case of heparinate of sodium) for which α_C and Λ_{Poly} increase with dilution, while $\Delta\lambda_{\text{Na}^+}^{\text{el}}$, $\Delta\lambda_p^{\text{el}}$, and $\beta^{\text{ir}} \rightarrow 0$; (b) the Manning concentration regime (it is the case of sodium polystyrene sulphonate) for which α_C , β^{ir} , and Λ_{Poly} remain sensibly constant with dilution, while $\Delta\lambda_{\text{Na}^+}^{\text{el}}$ and $\Delta\lambda_p^{\text{el}}$ decrease with concentration. It is important to underline that the ideal Manning behavior ($L_S/R_C \rightarrow \infty$) implies the restrictive conditions: $\alpha_C = \alpha_M = b_s/L_B$, $\beta^{\text{ir}} = 1/9$, and $\beta_p^{\text{df}} = 0$ (no dielectric friction: $v_p \tau > R_g$), while less restrictive conditions imply $\alpha_C = \text{constant}$, $\beta^{\text{ir}} = (\alpha_C/9\alpha_M)$, and $\beta_p^{\text{df}} \neq 0$. Only the sodium chondroitin sulfate presents an intermediate behavior between Ostwald concentration regime and Manning concentration regime with $\alpha_C \approx \alpha_M = 0.81$ and $\beta^{\text{ir}} \approx 0.13$. This mixed behavior is characterized by a slowly increasing of its equivalent conductivity with dilution.

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