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# Counterion Residence Time and Counterion Radial Diffusion in Rodlike Polyelectrolyte Solutions

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ABSTRACT: The cell model of a rodlike polyelectrolyte solution has been employed to evaluate the counterion residence time. This quantity has been compared with the dielectric relaxation time of the high-frequency dispersion observed in a well-defined rodlike polyelectrolyte solution. The agreement suggests that the high-frequency dielectric behavior of dilute polyelectrolyte solutions is characterized by counterion radial diffusion.

## Introduction

The peculiarity of some physical properties of aqueous solutions of polyelectrolytes is well-known[1] and various implications have been recently reviewed.[2] The unusual behavior of these systems results from strong interactions between counterions and polyion-ionizable groups and manifests in numerous physicochemical properties such as, for example, colligative and transport properties[3] and changes in the conformations of the macroion[4] or in specific counterion bindings.[5] Moreover, most of the physicochemical properties depend considerably on the presence or absence of an additional low molecular weight salt. Owing to the electrostatic character of these interactions, the dielectric properties of dilute polyelectrolyte solutions assume a role relevant to the investigation of counterion interactions.

Usually, these systems display, in the frequency range from $10^3$ to $10^7$ Hz, two adjacent dielectric dispersions, generally attributed to different molecular mechanisms. The large values of the dielectric increment of the low-frequency dispersion are explained by the theory of ionic polarization.[6]

On the other hand, the analysis of the quantitative character of the high-frequency region is more complex in some aspects. For example, Van der Touw and Mandel[7] have proposed a mechanism based on counterion fluctuation along certain characteristic distances of the linear, but flexible, polymer, and some valuable support for the existence of a subunit structure has been recently obtained from our own measurements.[8,9]

On the other hand, in terms of the linear lattice models developed by Minakata,[10] the high-frequency dispersion is due to counterion radial diffusion processes which reduce the relaxation time of ion fluctuation in the longitudinal ion motion. Moreover, the Maxwell–Wagner effect,[11] although it might explain some aspects, is unable to account for the main features of this dispersion, and, on the other hand, it is difficult to evaluate exactly the relaxation time from the bulk counterion diffusion model recently proposed to be a correcting factor on the dielectric increment.[12]

The aim of this paper is to calculate in an appropriate way the residence time $\tau$ of counterions for a polyelectrolyte cell model and to compare this value with the observed relaxation time for a typical polyelectrolyte solution. The comparison is restricted to a linear polyelectrolyte only, with three different counterions ($NH_4^+$, $Ca^{2+}$, and $Ba^{2+}$). Nevertheless, the reasonable agreement of the residence time with the observed dielectric relaxation time provides further support to attribute the high-frequency dispersion to the radial bulk counterion diffusion.

## Outline of the Theory

The simplest and most commonly adopted model for dilute solutions of rodlike polyelectrolytes is the Katchalsky cell model,[15] according to which each polyion is confined to an electroneutral cell of cylindrical symmetry, containing its counterions and, if any, appropriate quantities of added salt. The radius of the cell is given by

$$R = (\pi L C_n)^{-1/2}$$

where $C_n$ is the polyion number density and $L$ its overall length. The counterions are treated as point charges immersed in a continuous medium of dielectric constant $\epsilon$, and the polyion is assumed to be a cylinder of radius $a$ with a uniform surface charge density

$$\sigma = \frac{zeN}{2\pi a L}$$

where $N$ is the number of charges on the polyion total length.

The distribution of counterions in the neighborhood of each polyion is described by the Poisson–Boltzmann equation

$$\frac{1}{r}\frac{d}{dr}\left[r\frac{d\psi}{dr}\right] = -\frac{1}{\epsilon}\sum_i z_i e n_i(R) \exp\left\{-\frac{z_i e \psi}{k_B T}\right\} \qquad (1)$$

where the sum runs over all species of ions. $n_i(R)$ equals the average ion concentration of ions at the boundaries of the cell, where the potential is assumed to be zero.

In the presence of only counterions (due to the ionization of the charged groups of the polyion), if the potential $\Phi$ is scaled on $-ze/(k_B T)$ and the distance $u$ by the Debye screening length

$$K_D^{-1} = (e^2 z^2 \bar{n}/(\epsilon k_B T))^{-1/2}$$

where $\bar{n} = N/\pi L(R^2 - a^2)$ is the average counterion density, eq 1 becomes

$$\frac{d^2\Phi}{du^2} + \frac{1}{u}\frac{d\Phi}{du} = f e^{\Phi} \qquad (2)$$

where the counterion concentration at the cell boundary has been written as

$$n(R) = f\bar{n}$$

The constant $f$ must be chosen to satisfy the electroneutrality condition over to whole cell, i.e.

$$f = 2(l_B/l_\sigma)\Big/\int_{K_D a}^{K_D R} u e^{\Phi}\, du$$

where $l_\sigma = L/N$ and $l_B = e^2 z^2/(4\pi\epsilon k_B T)$ is the Bjerrum length, a natural length scale for polyelectrolyte solutions.

Following Stigter,[14] eq 2 can be rewritten as

$$\frac{d^2\Phi}{d\rho^2} = f e^{(2\rho + \Phi)}$$

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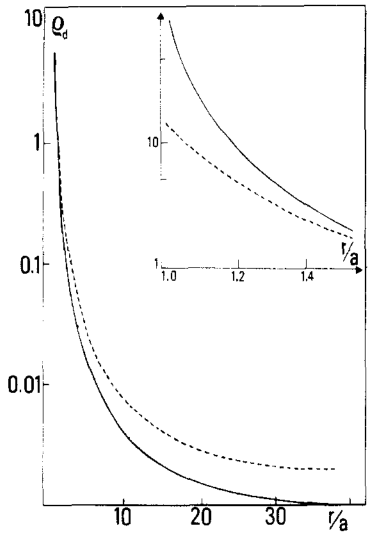

**Figure 1.** Dimensionless charge density $\rho_d = (K_Da)^2fe^{\Phi}$ predicted by the Poisson–Boltzmann equation as a function of $r/a$. The polyion concentration is $C_n = 10^{22}$ m$^{-3}$, the temperature $T = 20$ °C. Dotted line, in the absence of added salt, $C_s = 0$. Full line, in the presence of $CaCl_2$ electrolyte solution, $C_s = 10^{-4}$ mol/L.

with $\rho = \ln u$ and the integration proceeds by means of the Runge–Kutta method with the boundary conditions

$$\Phi|_{\ln K_DR} = 0$$

$$\left.\frac{d\Phi}{d\rho}\right|_{\ln K_Da} = -2\frac{l_B}{l_\sigma}$$

The numerical integration of eq 2 makes the potential and the local ion concentration known. Figure 1 shows the dimensionless charge density $\rho_d = (K_Da)^2fe^{\Phi}$ as a function of the distance $r/a$ from the polyion, for a typical value of the ratio $R/a$.

In the presence of an electrolyte, there will be three different contributions to the right-hand side of eq 1. Moreover, the distance $r$ cannot be scaled as a unique length. This means that eq 1 reads

$$\frac{d^2\Phi}{d\rho^2} = e^{2\rho}\{(K_Da)^2fze^{z\Phi} + \sum_1^2{}_j(K_{Dj}a)^2z_jf_je^{z_j\Phi}\}$$

with the conditions

$$f = \frac{1}{2}\left(\frac{R^2}{a^2} - 1\right)\Big/\int_0^{\ln R/a} e^{z\Phi+2\rho}\,d\rho$$

$$f_j = \frac{1}{2}\left(\frac{R^2}{a^2} - 1\right)\Big/\int_0^{\ln R/a} e^{z_j\Phi+2\rho}\,d\rho \qquad (j = 1, 2)$$

and

$$K_{Dj}^2 = \frac{e^2n_j}{\epsilon k_BTf_j} \qquad (j = 1, 2)$$

where $\sum^2{}_{1,j}ez_jn_j = 0$ to preserve the electroneutrality of the added electrolyte in the total cell volume.

The influence of the added salt on the counterion distribution is shown in Figure 1 (full line), where the screening effect of the salt is clearly evident. The mean residence time of a counterion in the cell can be defined as[15]

$$\tau = \int_0^\infty dt \int_a^r rp(r,t)\,dr$$

where $p(r,t)r\,dr$ is the probability of finding a counterion within $dr$ at a distance $r$ from the polyion axis at time $t$.

If the radial diffusion is governed by the Smoluchowski equation[16]

$$\frac{\partial}{\partial t}[p(r,t)] = \text{div}\left\{D\nabla_rp(r,t) + \frac{ze}{m}\frac{d}{dr}\psi(r)p(r,t)\right\}$$

where $D$ and $m$ are the diffusion coefficient and the mass of the ion, respectively, its direct integration, using the boundary condition

$$p(R,t) = 0$$

$$\frac{\partial}{\partial r}p(r,t)|_a + \frac{ze}{k_BT}\frac{d}{dr}\psi(r)|_ap(a,t) = 0$$

which implies that the polyion is impermeable to counterions, leads to the probability function, and the time $\tau$ can be consequently calculated according to

$$\tau = \frac{1}{D}\int_a^R \frac{e^{-\Phi}}{r}\left(\int_a^r se^{-\Phi}\,ds\right)^2\Big/\int_a^R re^{-\Phi}\,dr \qquad (3)$$

In the absence of added salt, $\tau$ can be obtained analytically, and it has been given previously.[15] On the other hand, in the presence of added salt only numerical solutions may be obtained. This definition of the residence time $\tau$ is closely linked to the time required for a counterion to diffuse over a cell of radius $R$, and we may conjecture that $\tau$ is simply related to the relaxation time measured by dielectric methods.

It must be noted that, once the value of the counterion diffusion coefficient is set, eq 3 contains no adjustable parameters, making the comparison appropriate.

## Comparison with Experiment

Recently, the dielectric dispersion of solutions of a well-characterized rodlike polyelectrolyte in the presence of different mono- and divalent counterions has been measured, and the relaxation times of the high-frequency dispersion have been evaluated.[8,9] The polyion employed, (carboxymethyl)cellulose (CMC) of well-defined molecular weight, should represent a good approximation to the cylindrical model and seems to be an appropriate model system, owing to its physicochemical properties, to use for a quantitative comparison with the theoretical predictions.

Three different counterions were studied. These ions have the following order in the lyotropic series: $NH_4^+ > Ca^{2+} > Ba^{2+}$, and interact differently with the CMC polyion.

The relaxation times of two different molecular weight polyions multiplied by the diffusion coefficient $D$, as a function of the polyion concentration in the interval from $3 \times 10^{-3}$ to $10^{-4}$ monomol/L at 20 °C in the presence of different cations as derived from the analysis of the dielectric spectra, are shown in Figures 2–4.

The details of sample preparation, dielectric measurements, and fitting procedure are described elsewhere.[9]

For the two CMC samples, taking the length of the cellulose repeating unit as 5.15 Å,[17] with degrees of substitution of 0.77 and 0.71, we used an average charge separation of 6.7 and 7.3 Å, respectively. The radius of the cylindrical polymer is assumed to be 7 Å.[18]

The diffusion coefficient $D$, in the limit of infinite dilution, has been calculated by the Nernst equation from the equivalent ionic conductivity.[19]

The results of the numerical analysis of eq 3 are shown in Figures 2–4. As can be seen, the agreement with our experimental results is good, especially at higher polyion concentration. It must be noted that the diffusion coefficient appearing in eq 3 may differ from that calculated

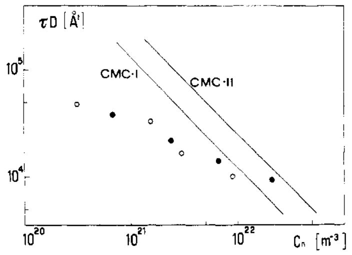

**Figure 2.** $\tau D$ as a function of the polyion concentration for the system $NH_4$–CMC. The concentration of the electrolyte solution ($NH_4Cl$) is $10^{-4}$ mol/L. (●) CMC-II MW = $1.98 \times 10^4$; (○) CMC-I MW = $4.4 \times 10^4$. The full lines represent the calculated values according to eq 3 for the two different molecular weight CMC samples.

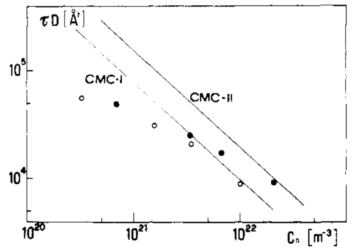

**Figure 3.** $\tau D$ as a function of the polyion concentration for the system Ca–CMC. The concentration of the electrolyte solution ($CaCl_2$) is $10^{-4}$ mol/L. (●) CMC-II MW = $1.98 \times 10^4$; (○) CMC-I MW = $4.4 \times 10^4$. The full lines represent the calculated values according to eq 3 for the two different molecular weight CMC samples.

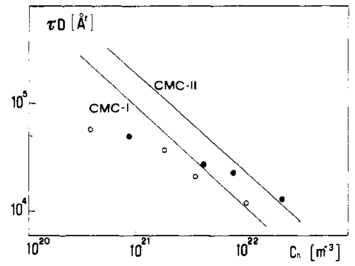

**Figure 4.** $\tau D$ as a function of the polyion concentration for the system Ba–CMC. The concentration of the electrolyte solution ($BaCl_2$) is $10^{-4}$ mol/L. (●) CMC-II MW = $1.98 \times 10^4$; (○) CMC-I MW = $4.4 \times 10^4$. The full lines represent the calculated values according to eq 3 for the two different molecular weight CMC samples.

from the conductivity of the bulk solution. In fact, the degrees of ion binding measured from ion concentration in ultrafiltration experiments[20] depende observably on the polyion species; polyions preferentially bind the less hydrated and presumably smaller counterions. In our case, both hydration and dimension vary considerably. Moreover, it has been emphasized[20] that for monovalent counterions ($Na^+$) the counterion activity coefficients are significantly larger than those predicted by condensation theory or by the Poisson–Boltzmann equation. The agreement is better in Ca–CMC and Ba–CMC samples in comparison with $NH_4$–CMC.

It must be noted that, in view of the assumptions made in the calculation of the potential, it would be more appropriate to limit our comparison to systems at infinite dilution, but, as pointed out by Scheraga et al.,[21] one should not be misled into thinking the cell model is equivalent to that for a single polyion in an infinite volume. It is difficult, on the other hand, to determine when the infinite dilution approximation is adequate.

The physical meaning of the residence time in the context of dielectric properties of rodlike polyelectrolytes should be better clarified also in order to understand whether its relation with the relaxation time measured by the dielectric method is justified.

The results presented here, however, offer valuable suggestions regarding this point of view, considering the high-frequency dielectric dispersion as due to the bulk counterion diffusion. The influence of different counterions should be further investigated and the possibility of a specific counterion binding mechanism, in addition to electrostatic binding, should be studied.

**Registry No.** CMC, 9000-11-7; $NH_4^+$, 14798-03-9; $Ca^{2+}$, 14127-61-8; $Ba^{2+}$, 22541-12-4.

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