Journal of Colloid and Interface Science **222,** 97–102 (2000)
doi:10.1006/jcis.1999.6615, available online at http://www.idealibrary.com on

Dielectric Relaxation Around a Charged Colloidal Cylinder in an Electrolyte

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Received June 24, 1999; accepted October 29, 1999

The polarizability and corresponding dielectric relaxation of the Debye–Hückel (DH) atmosphere surrounding a charged rod-like polyelectrolyte immersed in an ionic solution of a symmetrical electrolyte is determined following the method developed by J. A. Fornés [*Phys. Rev. E* 57, 2110 (1998)]. Several formulas are given to estimate the DH atmosphere parameters, namely, the polarizability at zero frequency, $\alpha(0)$, the relaxation time, τ, the cloud capacitance, $\mathbb{C}$, the average displacement of the ionic cloud, δ, the square root dipole moment quadratic fluctuation, $\langle p^2\rangle^{1/2}$, and the thermal fluctuating field, $\langle E^2\rangle^{1/2}$. The Poisson–Boltzmann equation is solved numerically to apply the theory to a highly charged polyelectrolyte such as DNA in solution, although formulas valid for the DH approximation are also given. A dispersion in the polarizability and correspondingly in the dielectric constant of these solutions in the microwave region is predicted. For instance, considering a DNA length of 1000 Å, with its reduced linear charge density $\xi_0 = 4.25$ and ionization factor $\gamma = 0.5$, immersed in a NaCl solution (40 mM), we predict a polarizability of the DH atmosphere at zero frequency $\alpha(0)$ of 1×10^{-33} Fm^2 ($\simeq 6.1 \times 10^6$) times greater than the mean value of the polarizability of water) and the corresponding fluctuating dipole moment p of 2.1×10^{-27} Cm ($\simeq$600 times greater than the permanent dipole moment of water molecule). The relaxation time and the average displacement of the ionic cloud are $\tau = 1.6$ ns and $\delta = 14.$ Å, respectively. This displacement is produced by the thermal fluctuating field, which, in this case, at room temperature is $\langle E^2\rangle^{1/2} = 2 \times 10^6$ V/m.

Key Words: **ionic dielectric relaxation; ionic polarization; cylindrical polyelectrolytes.**

I. INTRODUCTION

Since the pioneer works of Schwarz (1, 2), and Mandel (3) on the polarization of rod-like polyelectrolytes, a lot of work has been performed on this subject, basically because most of the biological macromolecules under physiological conditions are polyelectrolytes in solution and their biological activity depends on their physicochemical properties. Oosawa (4, 5) calculated the polarizability of a rold-like polyion considering the fluctuations of the counterion density. Manning (6) used his counterion condensation formalism to generalize Mandel's model for polarization; he also considered the effects of the Debye atmosphere in a steady electric field on the induced dipole moment in a formalism similar to the Onsager–Debye treatment (7) of conductance in ionic solutions (8). In a recent paper Mohanty and Zhao (9) (this paper is an excellent bibliography on polarization in polyelectrolytes) further generalized the Mandel–Manning theories to include low and high electric field without considering the response to an electric field of the Debye atmosphere and polarization of the condensed counterions perpendicular to the polyion axis. Fixman and Jagannathan estimated co-ion and condensed counterion polarization considering the ion atmosphere as producing convective effects on the polarization (10). Fornés (11), using the fluctuation–dissipation theorem, developed a simple method to estimate the longitudinal polarization of rod-like polyelectrolyte solutions, considering each charged group within the polyelectrolyte framework and its neighborhood as a circuit *RC*. In this paper we apply this method to estimate the Debye–Hückel (DH) atmosphere polarization perpendicular to the axis of a rod-like polyelectrolyte immersed in an ionic solution.

II. METHOD

We consider a rigid rod-like molecule or particle of radius a and length $L \gg a$, so that end effects may be neglected, with charge Q distributed uniformly over the surface with an electrical surface potential ψ_0 immersed in a solution of puntual ions of a symmetrical electrolyte of valence z with n ions per cubic meter. The law governing the potential profile and consequently the ionic distribution ("diffuse" layer) from the surface of the particle is given by the Poisson–Boltzmann (PB) equation,

$$\triangle\psi = \frac{2ze_0 n}{\varepsilon\varepsilon_0}\sinh\left(\frac{ze_0\psi}{kT}\right), \qquad [1]$$

where $\triangle$ is, in our case of cylinder symmetry, the radial part of the Laplace operator. Equation [1] can be written as

$$\frac{1}{x}\frac{d}{dx}\left(x\frac{dy}{dx}\right) = \sinh(y), \qquad [2]$$

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0021-9797/00 $35.00

where $y = ze_0\psi/kT$ and $x = \kappa r$ are the dimensionless potential and distance, respectively, r being the distance from the cylinder axis, perpendicular to the surface. At the surface of the cylinder $x = x_0 = \kappa a$ and $y = y_0 = ze_0\psi_0/kT$. The SI system of units was employed throughout, in Eq. [1]. ε_0 is the permittivity of vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}\ \mathrm{C}^2\ \mathrm{N}^{-1}\ \mathrm{m}^{-2}$), ε is the dielectric constant of the medium, e_0 is the electron charge ($e_0 = 1.602 \times 10^{-19}$ C) and κ, called the Debye–Hückel reciprocal length parameter (12), is given by

$$\kappa^2 = \frac{e_0^2}{\varepsilon\varepsilon_0 kT}\sum \eta_{i0} z_i^2 = \frac{2000 e_0^2 N_\mathrm{A}}{\varepsilon\varepsilon_0 kT}\left[\frac{1}{2}\sum c_i z_i^2\right]. \qquad [3]$$

The quantity $I = \frac{1}{2}\sum c_i z_i^2$ quantifies the charge in an electrolyte solution and is called the ionic strength after Lewis and Randall (13). In the case of a solution of a symmetrical (z–z) electrolyte we have

$$\kappa^2 = \frac{2(e_0 z)^2}{\varepsilon_0\varepsilon kT} n = \frac{2(e_0 z)^2}{\varepsilon_0\varepsilon kT} N_\mathrm{A} c 10^3, \qquad [4]$$

where k is the Boltzmann constant ($k = 1.381 \times 10^{-23}$ J/K), T is the absolute temperature, N_A is Avogadro's constant, and c is the solution concentration in moles per liter. For numerical integration of Eq. [2] see (15).

The contribution of the ionic cloud to the electrostatic potential at the rod surface will be (14, 15)

$$y_\mathrm{cloud}(x_0) = y(x_0) + 2z\xi\ \ln(x_0). \qquad [5]$$

We can then define the ionic cloud capacitance as

$$\mathbb{C} = \frac{Q}{\psi_\mathrm{cloud}(x_0)} = \frac{4\pi L\varepsilon_0\varepsilon\xi}{y(x_0) + 2z\xi\ln(x_0)}, \qquad [6]$$

where ξ is the reduced linear charge density over the rod surface (see next). In case the ratio of electrical to thermal energy of the ions is very small the DH approximation, ($ze_0\psi(r)/kT \ll 1$, or $y \ll 1$), Eq. [5] can be written as

$$\mathbb{C}_\mathrm{DH} = 2\pi L\varepsilon\varepsilon_0\left[\frac{K_0(x_0)}{x_0 K_1(x_0)} + \ln(x_0)\right]^{-1}, \qquad [7]$$

where $K_0(x_0)$ and $K_1(x_0)$ are the modified Bessel functions of zeroth and first order.

In our range of concentrations we approximate the relaxation time of the DH atmosphere by that given in Ref. (16):

$$\tau = \mathbb{R}(r)\mathbb{C}(r) = \varepsilon\varepsilon_0\rho, \qquad [8]$$

where $\mathbb{R}(r)$ is the resistance of the electrical path associated with the capacitance and ρ is the electrical resistivity, calculated by [see Ref. (16)]

$$\rho = \frac{1}{n(ze_0)^2\left[\left[1 - \frac{(ze_0)^2\kappa}{24\pi\varepsilon\varepsilon_0 kT}\frac{\sqrt{2}}{1+\sqrt{2}}\right]\frac{(D_0^+ D_0^-)}{kT} - \frac{\kappa}{3\pi\eta(1+\kappa g_i)}\right]}, \qquad [9]$$

where $D_0^\pm$ are the ionic diffusion constants, η is the viscocity of the solution, and a_i is the mean ion radius. Experimental values for ρ can also be used.

In Ref. (11) we obtained for the longitudinal polarizability $\alpha(0) = \mathbb{C}\delta^2$, where $\mathbb{C}$ is the total polyelectrolyte–ionic capacitance and δ the average displacement of the "bound" ions under the influence of the thermal fluctuating field. Any of the theories that predict $\alpha(0)$, δ, and relaxation time τ can be used to estimate $\mathbb{R}$ and $\mathbb{C}$; on the other hand, $\mathbb{R}$, $\mathbb{C}$, and δ can be obtained independently by modeling the system. Among the results is that the complex polarizability $\alpha(\omega)$,

$$\alpha(\omega) = \frac{\mathbb{C}\delta^2}{1+(\tau\omega)^2} + i\frac{-\tau\omega\mathbb{C}\delta^2}{1+(\tau\omega)^2}, \qquad [10]$$

where $\mathbb{C}$ is the total polyelectrolyte–ionic capacitance and δ the average displacement of the "bound" ions under the influence of the thermal fluctuating field. τ is the relaxation time of the fluctuation given by Eq. [11], and $\alpha(0)$ is given by

$$\alpha(0) = \mathbb{C}\delta^2. \qquad [11]$$

Correspondingly the real and imaginary components of the polarizability are

$$\alpha'(\omega) = \frac{\alpha(0)}{1+(\tau\omega)^2}, \quad \alpha''(\omega) = \frac{-\tau\omega\alpha(0)}{1+(\tau\omega)^2}. \qquad [12]$$

Also obtained were the following expressions for the dipole moment quadratic fluctuation, $\langle p^2\rangle$, and field, $\langle E^2\rangle$:

$$\langle p^2\rangle = \alpha(0)kT, \qquad [13]$$

$$\langle E^2\rangle = \frac{kT}{\alpha(0)} = \frac{kT}{\mathbb{C}\delta^2}. \qquad [14]$$

Both satisfied the classic analogy of the Heisenberg uncertainty principle:

$$\langle p^2\rangle\langle E^2\rangle = (kT)^2. \qquad [15]$$

III. POLARIZABILITY OF THE DEBYE–HÜCKEL ATMOSPHERE

We apply the preceding results to estimate the DH atmosphere polarizability $\alpha(0) = \mathbb{C}\delta^2$. We know that with the application of an electric field the center of charge of the central polyion is displaced from the center of charge of its cloud; this is analogous to what happens with a spherical ion giving rise to the egg-shaped ionic cloud [see, for instance, (14)]. The implication is that the ionic cloud is no longer symmetrical around the moving polyion; as a consequence a dipole is formed.

The central polyion practically loses its cloud if it diffuses to a distance δ during relaxation time τ of the fluctuation. In this way δ is given by

$$\delta = \tau v_{\mathrm{polyion}} = \tau \mu_{\mathrm{polyion}} \langle E^2 \rangle^{1/2}, \qquad [16]$$

where v_{polyion} and μ_{polyion} are the velocity and mobility of the polyelectrolyte in solution. From Eqs. [11], [14], and [16] we get

$$\alpha(0) = \tau \mu_{\mathrm{polyion}} [kT\mathbb{C}]^{1/2}. \qquad [17]$$

The mobility of a polyion of charge Q is given by (the formulas given by Ohshima (17–19) also can be used),

$$\mu_{\mathrm{polyion}} = \frac{Q}{f} = Q\left[\frac{D_{\mathrm{polyion}}}{kT}\right], \qquad [18]$$

where f (kg. s^{-1}) is the frictional coefficient of the polyion and D_{polyion} is its diffusion coefficient (m^2 s^{-1}). For a long rod the frictional coefficient is given by [see (20)]

$$f = \frac{3\pi\eta L}{2\ln(L/a) - 0.11}. \qquad [19]$$

Substituing μ_{polyion} given by Eq. [18] in Eq. [17], we get

$$\alpha(0) = \tau Q D_{\mathrm{polyion}} \left[\frac{\mathbb{C}}{kT}\right]^{1/2}. \qquad [20]$$

It is necessary to formulate a few definitions to put the equations into the current nomenclature of polyelectrolyte science, namely,

$$\lambda = \frac{Q}{L} = \frac{e_0}{b} = \left(\frac{e_0}{l_B}\right)\xi_0, \qquad [21]$$

where λ is the linear charge density, $b = L/N$ is the linear charge spacing, and N is the number of charged polymer groups. The Bjerrum length l_B is the distance at which the coulombic energy is equal to kT [($l_B = 7.13$ Å at 25°C in water)] for an excellent English reference on this subject, see (14)], namely,

$$l_B = \frac{e_0^2}{4\pi\varepsilon\varepsilon_0 kT} = \xi_0 b. \qquad [22]$$

The dimensionless ratio ξ_0, which is a reduced linear charge density, is particularly useful [a DNA molecule, for instance, has two phosphate charges each at a helical spacing of 3.37 Å, then $\xi_0 = l_B/b = 7.13 \times (2/3.37) = 4.23$]. As a consequence the surface charge density can be written as

$$\sigma = \frac{\lambda}{2\pi a} = \left(\frac{e_0}{2\pi a l_B}\right)\xi_0. \qquad [23]$$

For DNA, $a = 12.5$ Å, Eq. [23] gives $\sigma = 7.55 \times 10^{17}$ electric charges m^{-2}, which is 28 times less than that for a bidimensional array of Cu atoms.

Then, substituing $Q = L(e_0/l_B)\xi_0$ given by Eq. [21] into Eq. [20], we get

$$\alpha(0) = \tau L\left(\frac{e_0}{l_B}\right)\xi_0 D_{\mathrm{polyion}}\left[\frac{\mathbb{C}}{kT}\right]^{1/2}. \qquad [24]$$

In general in a polyelectrolyte the real charge is lessened by a factor γ because of the presence of counterions within the defining surface of the cylinder; correspondingly in the former equations ξ_0 has to be replaced by $\xi = \gamma\xi_0$.

In the range of validity of the DH approximation, Eq. [7] can be used to evaluate $\mathbb{C}_{\mathrm{DH}}$; on the contrary, the numerical solution of the Poisson–Boltzmann equation, through Eq. [6], has to be used.

To link microscopic parameters such as $\alpha(\omega)$ with macroscopic mensurable ones we make use of the results of the theory of electric polarization [see, for instance, (21)],

$$\varepsilon_0\varepsilon(\omega)E(\omega) = \varepsilon_0\varepsilon_{H_2O}E(\omega) + P(\omega), \qquad [25]$$

where $E(\omega)$ is the applied macroscopic field, and $P(\omega)$ is the polarization, which is given by

$$P(\omega) = \left(\frac{N_A}{V_M}\right)\alpha(\omega)F(\omega), \qquad [26]$$

where $F(\omega)$ is the “inner field,” which is the actual field experienced by the molecule, and V_M is the molar volume. From Eqs. [25] and [26] we obtain the relative increment in the dielectric constant:

$$\frac{\varepsilon(\omega) - \varepsilon_{H_2O}}{\varepsilon_{H_2O}} = B\left(\frac{N_A}{V_M}\right)\frac{1}{\varepsilon_0\varepsilon_{H_2O}}\alpha(\omega). \qquad [27]$$

With $B(\omega)$ given by

$$B(\omega) = \frac{F(\omega)}{E(\omega)}, \qquad [28]$$

where $E(\omega)$ is the applied field, B is usually a little larger than unity for a polar solvent (4).

Using the relations

$$\begin{aligned} \varepsilon(\omega) &= \varepsilon'(\omega) - i\varepsilon''(\omega), \\ \alpha(\omega) &= \alpha'(\omega) + i\alpha''(\omega), \end{aligned} \qquad [29]$$

then for the real and imaginary parts of the dielectric constant we have

$$\frac{\varepsilon'(\omega) - \varepsilon_{H_2O}}{\varepsilon_{H_2O}} = B\left(\frac{N_A}{V_M}\right)\frac{1}{\varepsilon_0\varepsilon_{H_2O}}\left[\frac{\alpha(0)}{[1 + (\tau\omega)^2]}\right], \qquad [30]$$

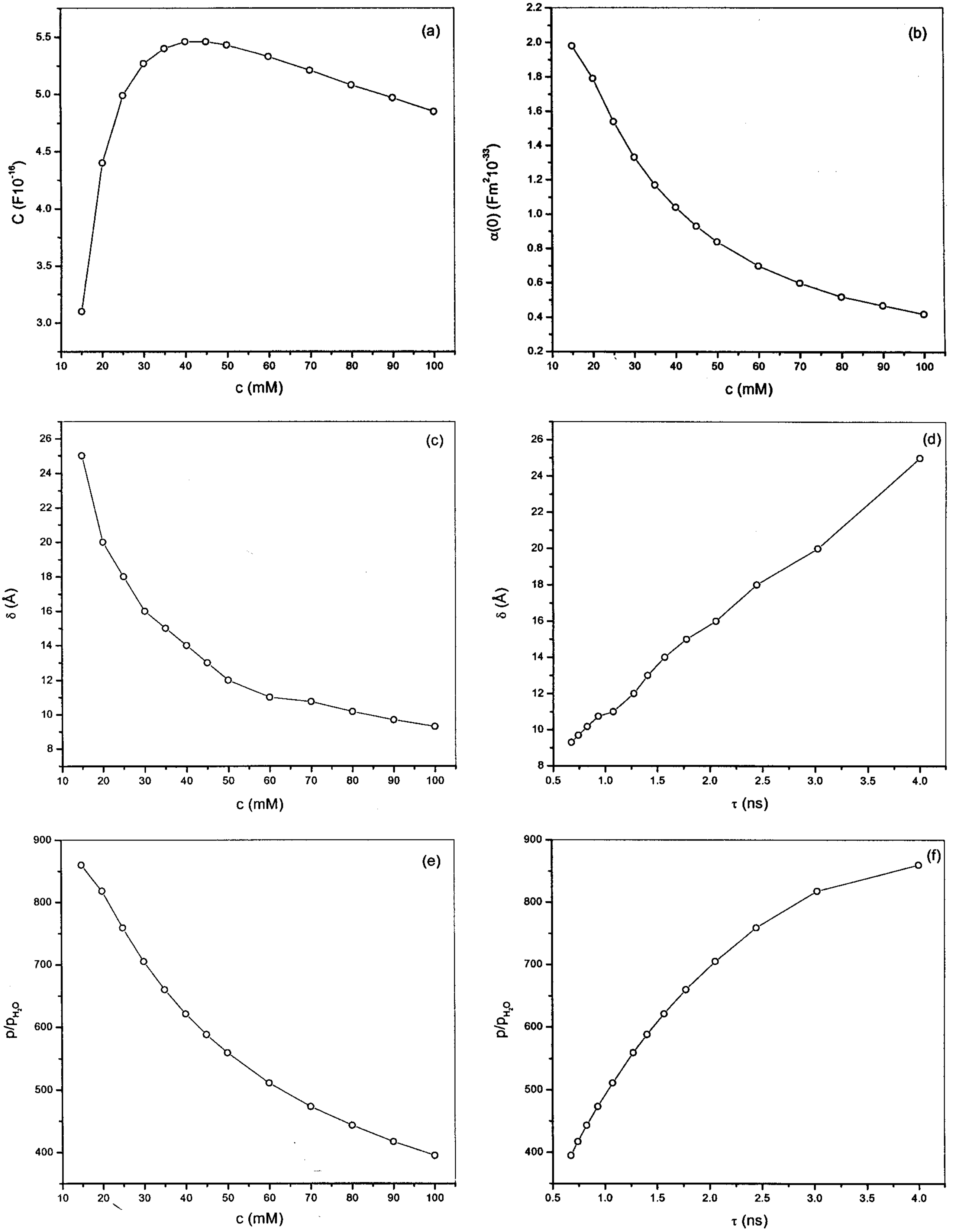

FIG. 1. Representation of the Debye–Hückel atmosphere parameters, in accordance with the values of Table 1, for DNA immersed in *c* mM NaCl solution in water.

$$\frac{\varepsilon''(\omega)}{\varepsilon_{\mathrm{H_2O}}} = -B\left(\frac{N_{\mathrm{A}}}{V_{\mathrm{M}}}\right)\frac{\omega}{\varepsilon_0\varepsilon_{\mathrm{H_2O}}}\left[\frac{\tau\alpha(0)}{[1+(\tau\omega)^2]}\right], \qquad [31]$$

with $\alpha(0)$ and τ given by Eqs. [24] and [8], respectively. In a more general actual experimental situation of a solution of volume V with N macroions, each one occupying an average volume v, we have to reemplace in Eqs. [30] and [31] the factor $N_{\mathrm{A}}/V_{\mathrm{M}}$ by $\phi/v = N/V$, with ϕ being the volume fraction.

Figure 2 is a representation of Eqs. [30] and [31] for a DNA solution at room temperature in water.

IV. RESULTS AND DISCUSSION

In Figures 1a–1f are plotted the results shown in Table 1. Figure 1a is a representation of Eq. [6] The capacitance is formed by the charged polyelectrolyte surface and the ionic atmosphere surrounding it. Figure 1b shows the plot of polarizability $\alpha(0)$ versus concentration (Eq. [24]); we observe that the decrease in relaxation time with concentration dominates polarization behavior. This is also manifested in the plot of the fluctuational dipole moment, $p/p_{\mathrm{H_2O}}$ (Fig. 1e, Eq. [13]). In Fig. 1c is shown the fluctuational displacement, δ, of the cloud with respect to the central polyion; we can also observe a decrease in δ with concentration because of the corresponding decrease in relaxation time with concentration (Eq. [16]). In Fig. 1d is the plot of δ versus τ, showing the linear relation. From Fig. 1f we observe the plot of $p/p_{\mathrm{H_2O}}$ versus relaxation time τ. The values for relaxation time are in accordance with those reported by Yoshida and Kikuchi (22), in their Metropolis Monte-Carlo Brownian dynamics simulation of the ion atmosphere polarization around a rod-like polyion. In Figs. 2a–2c are shown plots related to the dielectric dispersion due to relaxation of the DH cloud of a DNA

TABLE 1

Debye–Hückel Atmosphere Parameters by Numerical Solution of PB Equation for DNA Immersed in *c* mM NaCl Solution in Water[a]

x_0	c (mM)	$y(x_0)$	$\mathbb{C}$ (10^{-16} F)	$\alpha(0)$ (10^{-33} Fm^2)	δ (Å)	τ (ns)	$p/p_{\mathrm{H_2O}}$ [b]
0.50	15.0	8.90	3.10	1.98	25.	4.0	860.
0.58	20.0	6.52	4.40	1.79	20.	3.0	818.
0.65	25.0	5.55	4.99	1.54	18.	2.4	759.
0.71	30.0	4.96	5.27	1.33	16.	2.1	705.
0.77	35.0	4.55	5.40	1.17	15.	1.8	660.
0.82	40.0	4.23	5.46	1.04	14.	1.6	621.
0.87	45.0	3.98	5.46	0.93	13.	1.4	588.
0.92	50.0	3.77	5.43	0.84	12.	1.3	559.
1.00	60.0	3.45	5.33	0.70	11.	1.1	511.
1.08	70.0	3.20	5.21	0.60	11.	0.9	473.
1.16	80.0	3.01	5.08	0.52	10.	0.8	443.
1.23	90.0	2.84	4.97	0.47	10.	0.7	417.
1.30	100.0	2.71	4.85	0.42	9.	0.7	395.

[a] $L = 1000$ Å, $\xi_0 = 4.25$, $\gamma = 0.5$, $a = 12.5$ Å.

[b] Fluctuational dipole moment, p, in units of the dipole moment of water, $p_{\mathrm{H_2O}}$.

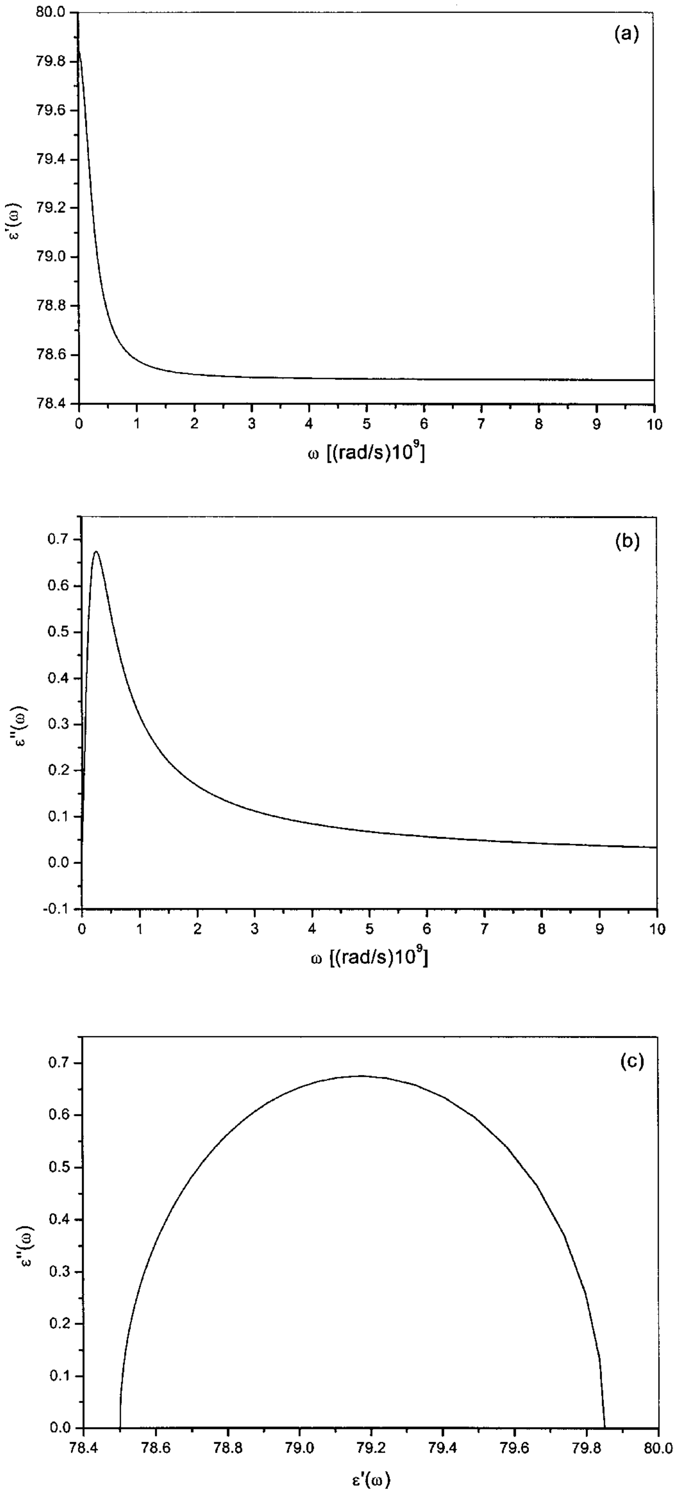

FIG. 2. (a) Representation of $\varepsilon'(\omega)$ from Eq. [30]. (b) Representation of $\varepsilon''(\omega)$ from Eq. [31]. (c) Cole–Cole plot for a DNA solution at room temperature in water: $B = 1$, $L = 1000$ Å, $\xi_0 = 4.25$, $\gamma = 0.5$, molecular weight $M_w = 10^6$, DNA concentration 10^{-2} mol/m^3 DNA in 15 mM NaCl solution, $\alpha(0) = 1.98 \times 10^{-33}$ Fm^2, $\tau = 4.0$ ns.

solution. For a DNA electrolyte solution (DNA length 1000 Å, DNA concentration 10^{-2} mol/m^3, electrolyte concentration 15 mM NaCl in water) a small increase in the dielectric constant is predicted at low frequencies with a relaxation time of 4. ns; this increase can be higher at lower concentrations. We want to emphasize that this relaxation is different from that caused by the bound ions, which is of the order of milliseconds and produces a polarizability parallel to the cylinder axis, $\alpha(0) \simeq 10^{-27}$ Fm^2, described in Ref. (11). The DH atmosphere relaxation is in the microwave region of the spectrum and could be measured by conventional techniques such as microwave bridges and microwave resonant cavities (23, 24). As far as we know, DH atmosphere parameters and their influence on dielectric relaxation for DNA solutions in this concentration range have not been treated by other authors. We hope that these results will stimulate new experiments.

ACKNOWLEDGMENT

This work was partially supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil).

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