Macromolecules **1991,** *24,* 3857-3865

Theory on the Relation between the Dielectric Relaxation and the Polyion Mobility Relaxation in Polyelectrolyte Solutions

Kohzo Ito*

Research Institute for Polymers and Textiles, Tsukuba, Ibaraki 305, Japan

Reinosuke Hayakawa

Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Received November 21, 1990

ABSTRACT: The effect of polyion mobility on the complex conductivity σ^* (or the complex dielectric constant ϵ^*) in polyelectrolyte solutions is theoretically treated by using the conductivity formalism instead of the conventional dipole moment formalism. The qualitative consideration of the relation between σ^* (or ϵ^*) and the complex mobility U^* of the polyion leads us to the conclusion that the relaxations in σ^*, ϵ^*, and U^* commonly arise from competition between the frictional and Coulombic attractive forces, which have different frequency dependences. As a result, σ^*, ϵ^*, and U^* are closely related to each other with the same order of relaxation times. This conclusion is confirmed by quantitative calculations based on the cell model, which show that σ^* is proportional to U^* in a solution without added salts. The present theory clearly demonstrates the significance of the polyion mobility in the dielectric relaxation, particularly in the polyelectrolyte solution without added salts.

1. Introduction

It is widely known that part of the counterions in the polyelectrolyte solution are bound to the polyion by the Coulombic attractive force, losing their activities and contributing to the electric polarizability.[1,2] Dielectric relaxation spectroscopy gives us useful information on the dynamic behavior of the bound counterions[3] that is not obtainable from the usual static or stationary techniques for measuring the osmotic pressure, the dc conductivity, and so on. The experimental results[4-6] of the dielectric relaxation in the semidilute region of the linear polyelectrolyte solution exhibit two kinds of relaxations, the low-frequency (LF) and high-frequency (HF) ones. Recent development of the measurement techniques for the dielectric relaxation[6] and the frequency domain electric birefringence[7] has given us a detailed picture of the LF and HF relaxations in polyelectrolyte solution. Both relaxations are ascribed to the anisotropic fluctuation or movement of counterions in the solution: The LF relaxation is attributable to the movement of the tightly bound counterions along the long axis of the polyion, while the HF one is ascribable to the movement of the loosely bound counterions in the direction perpendicular to the polyion axis within the range of the interpolyion distance.

From the theoretical point of view, however, the electrical dynamics of a linear polyelectrolyte solution still remains ambiguous in spite of many theoretical studies.[3] Most of the theories are based on all or some of three unreliable assumptions, i.e., the two-phase model, the dipole moment formalism, and the immobility of polyions.

The two-phase model, first of the three, in which the polyelectrolyte solution is divided into the bound and free phases, has an essential ambiguity that the boundary between the two phases is not clearly defined. Therefore, the dielectric increment $\Delta\epsilon$ theoretically estimated from this model contains some adjustable parameters such as the size of the bound phase.[8]

Second, the complex polarizability α^* or the complex dielectric constant ϵ^* in the polyelectrolyte solution has been defined in most cases by using the electric dipole moment due to the distortion effect of the applied electric field on the distribution of the bound counterions, which we call the dipole moment formalism. In the polyelectrolyte solution, however, this formalism cannot give proper definition of ϵ^* since the counterions in the solution contribute to the conductivity as well as the polarizability. In order to treat properly the conductivity and polarizability produced by the counterions, we need to introduce the conductivity formalism where ϵ^* is defined operationally by using the complex conductivity σ^* as[9]

$$\sigma^* = \sigma(0) + i\omega\epsilon_0\epsilon^* \tag{1.1}$$

Here $\sigma(0)$ is the dc conductivity, ω the angular frequency of the applied electric field, and ϵ_0 the vacuum permittivity. This formalism is consistent with actual procedures in the dielectric relaxation measurement for the polyelectrolyte solution because we experimentally obtain ϵ^* from the specimen admittance proportional to σ^*. Thus, we should employ the conductivity formalism instead of the dipole moment formalism in both the theoretical and experimental treatments of ϵ^* for the polyelectrolyte solution.

Last of the three, the assumption of the immobile polyion in the estimation of σ^* or ϵ^*, is also doubtful since the experimental results of $\sigma(0)$ show a definite contribution of the polyion to $\sigma(0)$ in the linear polyelectrolyte solution without added salts.[10] Imai and Iwasa[11] calculated the polyion mobility (electrophoretic mobility) $U(0)$ in the low-frequency limit, which contributes to $\sigma(0)$. However, the influence of the complex mobility U^* of the polyion on σ^* under the ac electric field with an arbitary frequency has not been discussed so far.

The purpose of this study is to treat σ^* or ϵ^* of the polyelectrolyte solution theoretically by using the conductivity formalism and properly taking into account the polyion mobility. The remainder of the paper is organized as follows. In section 2, we consider the relation between σ^* (or ϵ^*) and U^* in a general and qualitative manner. In section 3 are presented the model and fundamental equations for a quantitative evaluation of σ^*. In section 4, we obtain the relation between σ^* and U^* in the case of the solutions both without and with added salts. In section 5, the relation between ϵ^* and the susceptibility

0024-9297/91/2224-3857$02.50/0

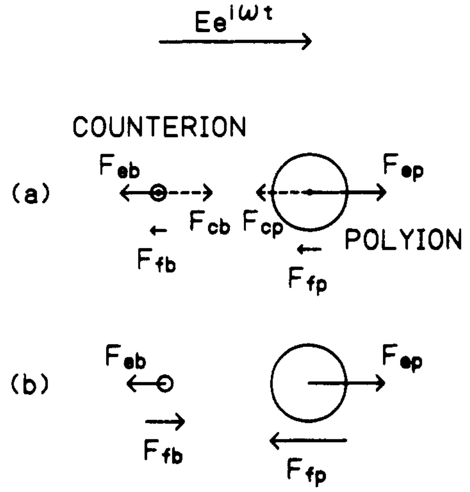

Figure 1. (a) In the low-frequency limit of a dielectric relaxation, the external electric force $F_{ep} = QEe^{i\omega t}$, the Coulombic attractive force F_{cp}, and the frictional force F_{fp}, exerted on the polyion, are balanced with each other. Similarly, the external electric force $F_{eb} = -qEe^{i\omega t}$, the Coulombic attractive force F_{cb}, and the frictional force F_{fb}, exerted on the bound counterions, are balanced with each other. (b) In the high-frequency limit where the contributions of the Coulombic attractive forces F_{cp} and F_{cb} are negligible, F_{ep} is balanced with F_{fp} and F_{eb} is with F_{fb}.

χ^* is given for the solution without added salts, which clearly indicates the difference between the present treatment and the conventional one based on the dipole moment formalism. Finally, in section 6, we discuss the applicability of the present theory to some specific cases of the polyelectrolyte solutions.

2. General Consideration

Prior to a quantitative evaluation, we consider the relation between σ^* (for ϵ^*) and U^* of the polyelectrolyte solution without added salts in a qualitative manner. We suppose the counterions with a negative charge of $-q$ and a friction constant of ζ, dissociated from the polyion with a positive charge of Q and a friction constant of ζ_P, and divide them into two groups, N_B bound counterions and N_F free ones. Here, Q is equal to $(N_B + N_F)q$ and q is the elementary charge. The bound counterions do not contribute to the dc conductivity, that is, they move together with the polyion under the dc electric field. This is due to the Coulombic attractive force F_{cb}, exerted on the bound counterions by the polyion, as shown in Figure 1a. The free counterions not influenced by F_{cb}, on the other hand, move in the opposite direction to the polyion under the dc field and thus contribute to the dc conductivity independently of the polyion. Hence, the difference between the bound and free counterions in the contribution to the dc conductivity is ascribed to the Coulombic attractive force F_{cb} in the low-frequency limit.

Next, we will consider the effect of F_{cb} on the movement of the bound counterions under the ac electric field. When the electric field $Ee^{i\omega t}$ with the small amplitude E and the angular frequency ω is applied to the polyelectrolyte solution, the external electric force $F_{ep} = QEe^{i\omega t}$ exerted on the polyion moves the polyion at a velocity of $U^*Ee^{i\omega t}$ and, at the same time, produces the displacement $x = w^*Ee^{i\omega t}$ of the bound counterions relative to the polyion in cooperation with the external electric force $F_{eb} = -qEe^{i\omega t}$ on the bound counterions. Here, U^* is the complex mobility of the polyion, w^* is the complex coefficient, which represents the relative displacement induced by unit electric field, and nonlinear terms of E are neglected. The Coulombic attractive force F_{cb} arises from the relative displacement x of the bound counterions and is expressed as

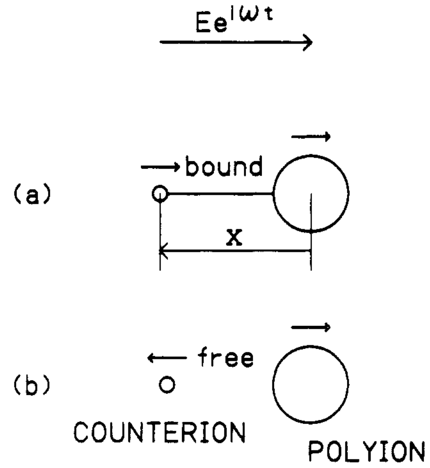

Figure 2. Movement of the polyion and counterions (a) in the low-frequency limit and (b) in the high-frequency limit.

$$F_{cb} = -\partial\psi(x)/\partial x \tag{2.1}$$

where $\psi(x)$ represents an effective (i.e., self-consistent) electric potential for the bound counterion. In the low-frequency limit, as shown in Figure 1a, F_{cb} acts in the opposite direction to F_{eb} and is larger than F_{eb} in its magnitude. The difference between F_{cb} and F_{eb} is balanced by the other force, the frictional one F_{fb} exerted on the bound counterion from the solvent. The force F_{fb} is in proportion to the velocity of the bound counterion relative to the solvent and hence increases with ω as

$$F_{fb} = \zeta(i\omega w^* + U^*)Ee^{i\omega t} \tag{2.2}$$

where the first term in parentheses corresponds to the velocity of the bound counterion relative to the polyion and the second term represents the polyion velocity. Equation 2.2 indicates that F_{cb} becomes negligible compared with F_{fb} as ω increases since F_{cb} given by eq 2.1 is explicitly independent of ω. Thus, the balance of three forces F_{eb}, F_{cb}, and F_{fb} for the frequency-independent amplitude E of the external electric field results in a distinct frequency dependence of F_{cb}; that is, the magnitude of F_{cb} is the largest in the low-frequency limit, decreases with increasing ω, and vanishes in the high-frequency limit, because of the monotonic decrease of x with increasing ω. As a result, in the high-frequency limit as shown in Figure 1b, the bound counterions are not affected by F_{cb} as well as the free counterions. This frequency dependence of the Coulombic attractive force F_{cb} results in the frequency dispersion of the conductivity, polyion mobility, and polarizability in the polyelectrolyte solution as will be seen in the following.

In the low-frequency limit, both the polyion and the bound counterions move in a body under the electric field as schematically shown in Figure 2a. Hence, the polyion mobility $U(0)$ in the low-frequency limit is estimated as $(Q - N_Bq)/(\zeta_P + N_B\zeta)$, equal to the mobility of a body with a smaller effective charge $Q - N_Bq$ and larger friction constant $\zeta_P + N_B\zeta$ than the polyion alone. This leads us to the evaluation of the dc conductivity $\sigma(0)$ as $\sigma(0) = [(Q - N_Bq)^2/(\zeta_P + N_B\zeta) + N_Fq^2/\zeta]/V$, where V is the solution volume per polyion. Furthermore, the electric polarization proportional to the relative displacement x of the bound counterions is induced in the low-frequency limit.

In the high-frequency limit, on the other hand, the movements of the polyion and bound counterions become independent of each other owing to the absence of F_{cb} as

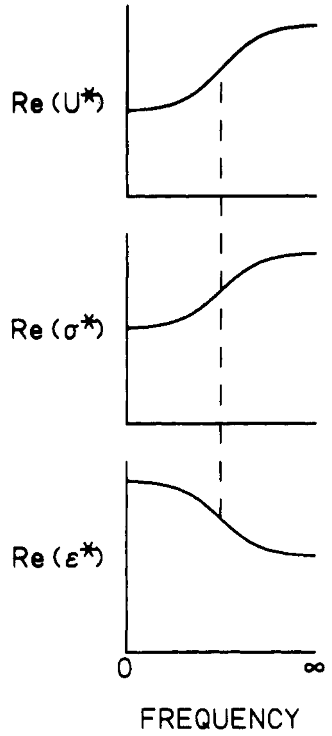

Figure 3. Frequency dependence of the real parts of U^*, σ^*, and ϵ^*.

schematically shown in Figure 2b. Thus, the bound counterions behave as if they were free ones, which produce no polarization, and the polyion has the mobility $U(\infty) = Q/\zeta_P$ larger than $U(0)$ because the higher charge and the smaller friction constant result in a larger mobility. Also, the conductivity $\sigma(\infty)$ in the high-frequency limit is estimated as $\sigma(\infty) = [Q^2/\zeta_P + (N_B + N_F)q^2/\zeta]/V$, which is larger than $\sigma(0)$.

In consequence, as schematically shown in Figure 3, the complex mobility U^* of the polyion is expected to show a frequency dependence of the relaxational type with the relaxation time τ of the same order as σ^* and ϵ^* (or the polarizability relaxation). In other words, the relaxations of the polyion mobility U^*, the conductivity σ^*, and the dielectric constant ϵ^* in the polyelectrolyte solution commonly arise from competition between the Coulombic attractive and frictional forces, which have different frequency dependences. This close relation among U^*, σ^*, and ϵ^* is also derived from a simple spring model, as will be described in Appendix A where the Coulombic interaction between the polyion and the bound counterions is replaced with the effective spring force. Incidentally, the electrophoretic effect, which has been neglected in this section, has little influence on the qualitative conclusion above, as will be mentioned in Appendix B. The qualitative conclusion will be confirmed quantitatively in the following sections.

3. Fundamental Equations for Quantitative Arguments

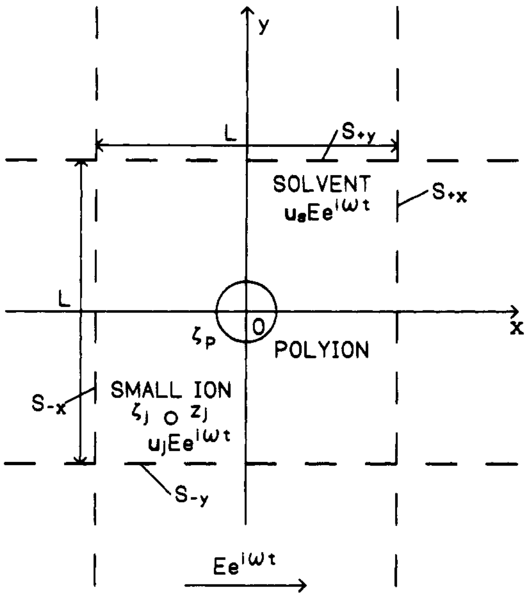

Figure 4. Cell model where cubic free volumes with the edge L are arranged periodically in a three-dimensional space.

For quantitative arguments of σ^* and U^* in solution, we adopt the cell model in order to avoid the difficulty in the boundary conditions in a polyelectrolyte solution without an excess amount of added salts. This model, originally used by Imai and Iwasa[11] in the estimation of $U(0)$ and $\sigma(0)$, assumes that cubic cells (free volumes) with edge length L are arranged periodically in the three-dimensional space as shown in Figure 4 and that each cell satisfies the condition of electrical neutrality. When the external electric field $Ee^{i\omega t}$ with an amplitude of E and an angular frequency of ω is applied to the solution along the x-axis, the polyion with the friction constant ζ_P moves along the x-axis with the velocity $U^*Ee^{i\omega t}$. We adopt in the following, as the origin of coordinates, the center O of a cell, which moves with the same velocity as the polyion. Then, in this coordinate system, the polyion always stands still and the solvent moves with the velocity vector $\mathbf{u}_s(x,y,z)Ee^{i\omega t}$. As long as the nonlinear terms with respect to E are negligible, the movement of the coordinate system has no influence on the conductivity or polarizability in an electrically neutral system. In Figure 4, $\mathbf{u}_j(x,y,z)Ee^{i\omega t}$ is the velocity vector of the jth kind of small ion with a valence z_j and a friction constant ζ_j. The symbols $S_{\pm x}$, $S_{\pm y}$, and $S_{\pm z}$ represent the cell surfaces perpendicular to the x-, y-, and z-axes, respectively. The solvent dielectric constant ϵ_s is assumed to be uniform over the whole cell.

The fundamental equations are the following three: the equation of continuity

$$\partial F_j/\partial t + \mathrm{div}\,(F_j\mathbf{u}_jEe^{i\omega t}) = 0 \qquad (3.1)$$

the equation of the balance for the frictional, diffusional, and Coulombic forces exerted on the small ions of the jth kind

$$\zeta_j(\mathbf{u}_j - \mathbf{u}_s)Ee^{i\omega t} = -kT\,\mathrm{grad}\left(\ln F_j + \frac{z_jq}{kT}\Phi\right) \qquad (3.2)$$

and the Poisson equation

$$\nabla^2\Phi = -\frac{q}{\epsilon_s\epsilon_0}\left(\sum_j z_jF_j + F_P\right) \qquad (3.3)$$

where F_j is the distribution function of the small ions of the jth kind, Φ the electric potential, F_P the distribution function of the polyion, kT the thermal energy, and q the elementary charge.

When E is small, F_j and Φ are expressed as

$$F_j(x, y, z, t) = F_{j0}(1 + f_jEe^{i\omega t}) \qquad (3.4)$$

$$\Phi = \Phi_0 + (\phi - x)Ee^{i\omega t} \qquad (3.5)$$

where F_{j0} and Φ_0 are the distribution function and the electric potential in the absence of the applied electric field and f_j and ϕ represent the distortion induced by the applied electric field. In the absence of applied electric field, the fundamental equations (3.2) and (3.3) reduce to the Poisson–Boltzmann equation, from which we obtain the relation between F_{j0} and Φ_0 as

$$F_{j0} = n_j V \exp\left(\frac{z_j q}{kT}\Phi_0\right) \Big/ \int \exp\left(\frac{z_j q}{kT}\Phi_0\right) \mathrm{d}V \qquad (3.6)$$

Here, the integral is performed over the cell volume equal to L^3 and the number concentration n_j of the small ions of the jth kind is defined by

$$n_j = \int F_{j0}\,\mathrm{d}V/V \qquad (3.7)$$

Substituting eqs 3.4 and 3.5 into eq 3.2 and pulling out the components proportional to E, we have

$$\zeta_j(\mathbf{u}_j - \mathbf{u}_s)Ee^{i\omega t} = z_j q \operatorname{grad} xEe^{i\omega t} - \operatorname{grad} \psi_j \qquad (3.8)$$

where the effective potential ψ_j affecting the jth small ion is defined by

$$\psi_j = [kTf_j + z_j q\phi]Ee^{i\omega t} \qquad (3.9)$$

The left-hand side in eq 3.8 means the frictional force F_{fb} exerted on the small ion in Figure 1, and the first term of the right-hand side represents the force F_{eb} due to the external electric field. The remainder of the right-hand side arises from the distortions f_j of the small ion distribution and ϕ of the electric potential as seen in eq 3.9 and hence corresponds to the Coulombic attractive force F_{cb} in section 2, although the diffusional force is also included in this case. Equation 3.9 gives us the specific form of the effective potential ψ in eq 2.1, using the distortions f_j and ϕ. As a result, eq 3.8 supports our picture for the balance among F_{eb}, F_{cb}, and F_{fb} in the low- and high-frequency limits mentioned in section 2.

In the cell model, we alternatively assume the x-axial symmetry of a polyion or a smaller size of the polyion compared with that of the cell. Then a set of boundary conditions are derived from the symmetry and periodicity of F_j and Φ. Among them, the following will be used in the subsequent calculations:

$$\frac{\partial \Phi_0}{\partial x}\Big|_{S_{\pm x}} = \frac{\partial \Phi}{\partial y}\Big|_{S_{\pm y}} = \frac{\partial \Phi}{\partial z}\Big|_{S_{\pm z}} = 0 \qquad (3.10)$$

$$\frac{\partial \phi}{\partial x}\Big|_{S_{+x}} = -\frac{\partial \phi}{\partial x}\Big|_{S_{-x}} \qquad (3.11)$$

$$\frac{\partial \Phi}{\partial y}\Big|_{S_{+x}} = \frac{\partial \Phi}{\partial y}\Big|_{S_{-x}},\quad \frac{\partial \Phi}{\partial z}\Big|_{S_{+x}} = \frac{\partial \Phi}{\partial z}\Big|_{S_{-x}} \qquad (3.12)$$

$$F_j(L/2, y, z) = F_j(-L/2, y, z) \qquad (3.13)$$

4. Relation between σ^* and U^*

The complex conductivity σ^* is defined as the integral of the true current density $\mathbf{J}$ and the polarization current density $\partial\mathbf{D}/\partial t$ over the whole cell as

$$\sigma^* = \int \left(\mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}\right)_x \mathrm{d}V/(VEe^{i\omega t}) \qquad (4.1)$$

where $\mathbf{J}$ and the electric displacement $\mathbf{D}$ are expressed as

$$\mathbf{J} = \sum_j z_j q F_j \mathbf{u}_j Ee^{i\omega t} \qquad (4.2)$$

$$\mathbf{D} = -\epsilon_s \epsilon_0 \operatorname{grad} \Phi \qquad (4.3)$$

and the suffix x represents the vector component along the x-axis. By substituting eqs 4.2 and 4.3 into eq 4.1 and using eq 3.5, we have

$$\sigma^* = \sum_j z_j q \int F_{j0} u_{jx}\,\mathrm{d}V/V + i\omega\epsilon_s\epsilon_0\left(1 - \int \frac{\partial \phi}{\partial x}\,\mathrm{d}V/V\right) \qquad (4.4)$$

Since the electric potential difference between S_{+x} and S_{-x} is equal to $LEe^{i\omega t}$, the integral in the bracket of eq 4.4 vanishes and eq 4.4 is reduced to

$$\sigma^* = \sum_j z_{jq} \int F_{j0} u_{jx}\,\mathrm{d}V/V + i\omega\epsilon_s\epsilon_0 \qquad (4.5)$$

On the other hand, we rewrite eq 4.1 as

$$\sigma^* = \sum_j z_j q \int xF_{j0} u_{jn}\,\mathrm{d}S/V + i\omega\epsilon_s\epsilon_0\left(1 - \int x \operatorname{grad}_n \phi\,\mathrm{d}S/V\right) \qquad (4.6)$$

by replacing the volume integral over the cell with the surface integral on the cell and using eqs 3.4 and 3.5. The suffix n in eq 4.6 represents the vector component in the direction outwardly normal to the cell surface.

The electrical susceptibility χ^* due to the distortion of small ion distribution in the cell, which corresponds to the electrical polarizability in section 2, is given as

$$\chi^* = \sum_j z_j q \int xF_j\,\mathrm{d}V/(\epsilon_0 VEe^{i\omega t}) = \sum_j z_j q \int xF_{j0}f_j\,\mathrm{d}V/(\epsilon_0 V) \qquad (4.7)$$

By use of eq 3.3, χ^* in eq 4.7 is rewritten as

$$\chi^* = -\epsilon_s\left[\int x \operatorname{grad}_n (\phi - x)\,\mathrm{d}S - \int \frac{\partial(\phi - x)}{\partial x}\,\mathrm{d}V\right]/V = -\epsilon_s\left[\int x \operatorname{grad}_n \phi\,\mathrm{d}S - \int \frac{\partial \phi}{\partial x}\,\mathrm{d}V\right]/V = -\epsilon_s \int x \operatorname{grad}_n \phi\,\mathrm{d}S/V \qquad (4.8)$$

which indicates that χ^* due to the distortion of the small ion distribution is expressed in terms of the electric field on the electrodes. Substituting χ^* into eq 4.6, we get

$$\sigma^* = \sum_j z_{jq} \int xF_{j0} u_{jn}\,\mathrm{d}S/V + i\omega\epsilon_0(\epsilon_s + \chi^*) \qquad (4.9)$$

As shown in Appendix C, the Poisson equation (3.3) and the boundary conditions (3.10)–(3.13) give us the relation with respect to U^* as

$$\sum_j \zeta_j \int (u_{jx} - u_{sx})F_j\,\mathrm{d}V + \zeta_{\mathrm{P}} U^* = 0 \qquad (4.10)$$

Here the friction constant ζ_{P} of the polyion depends on ω since the frequency-dependent Coulombic attractive force between the polyion and the bound counterions influences the electrophoretic effect on the polyion (the electrophoretic acceleration) as mentioned in Appendix B. Multiplying eq 3.1 by $\zeta_j x$ and summing up with respect to j after the integral over the whole cell, we obtain

$$\sum_j \zeta_j\left[i\omega \int xF_{j0}f_j\,\mathrm{d}V + \int xF_{j0}u_{jn}\,\mathrm{d}S - \int F_{j0}u_{jx}\,\mathrm{d}V\right] = 0 \qquad (4.11)$$

Combining eq 4.10 with eq 4.11, we get the relation

$$\sum_j \zeta_j [i\omega \int x F_{j0} f_j \, \mathrm{d}V + \int x F_{j0} u_{jn} \, \mathrm{d}S] = \sum_j \zeta_j \int F_{j0} u_{sx} \, \mathrm{d}V - \zeta_P U^* \quad (4.12)$$

A. Without Added Salts. In the polyelectrolyte solutions with no added salts (i.e., containing a single species of counterion), the combination of eqs 4.5 and 4.10 yields

$$\sigma^* = i\omega\epsilon_s\epsilon_0 + (zq/\zeta V)[\zeta \int F_0 u_{sx} \, \mathrm{d}V - \zeta_P U^*] \quad (4.13)$$

where z and ζ are the valence and friction constant, respectively, of the counterion and F_0 is the distribution function of the counterion in the absence of the applied electric field. Equation 4.13 indicates a close relationship between σ^* and U^*, which is consistent with the qualitative consideration in section 2.

After Imai and Iwasa,[11] we assume the electrophoretic effect to be negligible, which means that the counterion has no influence on the solvent stream and that the polyion is free draining. In this case, u_{sx} becomes a constant equal to $-U^*$ because the solvent always stands still in the laboratory coordinate system, and ζ_P is independent of ω. Thus, we get a simple relation between σ^* and U^* from eq 4.13 as

$$\sigma^* = i\omega\epsilon_s\epsilon_0 - zq[n + \zeta_P/(\zeta V)]U^* \quad (4.14)$$

where n represents the average number concentration of counterions. Equation 4.14 clearly indicates that σ^* has the same frequency dependency as U^* apart from the first term in the right-hand side. Also, eq 4.14 agrees with eq A7 in Appendix A, derived from the spring model, which suggests that the dynamic behavior in the polyelectrolyte solution is described well by the spring model. Since U^* may be measured in the low-frequency range by using the electrophoretic light scattering (EPLS),[12] the present theory suggests that the dielectric relaxation spectroscopy is closely related to EPLS. If a relaxation in U^* is observed in EPLS, the relaxation time should be of the same order as that in σ^* or ϵ^*.

B. With Added Salts. In the case of the solution with added salts, we employ the assumption that the size of the polyion is much smaller than that of the cell, which results in the following relations:

$$\mathrm{grad}_n f_j|_{S_{\pm x,\pm y,\pm z}} = 0 \quad (4.15)$$

$$\int x F_{j0} u_{sn} \, \mathrm{d}S = n_{jF} \int x u_{sn} \, \mathrm{d}S \simeq -n_{jF} U^* V \quad (4.16)$$

$$\int x F_{j0} \, \mathrm{grad}_n \, \phi \, \mathrm{d}S = -n_{jF} \chi^* V/\epsilon_s \quad (4.17)$$

Here n_{jF} is the average number concentration of the free small ions of the jth kind defined by

$$n_{jF} = \int F_{j0} \, \mathrm{d}S/S \quad (4.18)$$

where S represents the surface area of the cell equal to $6L^2$. Substituting eq 3.8 into eq 4.9 and using eqs 4.15–4.17 give us

$$\sigma^* = [i\omega\epsilon_s\epsilon_0 + \sum (z_j^2 q^2/\zeta_j) n_{jF}](1 + \chi^*/\epsilon_s) - \sum z_j q n_{jF} U^* \quad (4.19)$$

where the last term in the right-hand side represents the contribution of U^* to σ^* and becomes negligible compared with the contribution of the small ions in the limit of excessive salts. In this case, eq 4.19 reduces to the result by DeLacy and White.[9]

Assuming again that the electrophoretic effect is negligible and using eqs 4.15–4.17 after the substitution of eq 3.8 into eq 4.12, we obtain U^* by

$$U^* = \frac{-\sum_j z_j q n_{jF}(1 + \chi^*/\epsilon_s)V - i\omega \sum_j \zeta_j \int x F_{j0} f_j \, \mathrm{d}V}{\zeta_P + V \sum_j \zeta_j (n_j - n_{jF})} \quad (4.20)$$

In the low-frequency limit, eq 4.20 reduces to

$$U(0) = -\sum_j z_j q n_{jF}(1 + \chi(0)/\epsilon_s)V/[\zeta_P + V \sum_j \zeta_j (n_j - n_{jF})] \quad (4.21)$$

where $\chi(0)$ is the low-frequency limit of χ^*. If $\chi(0)$ is negligibly small compared with ϵ_s in the very dilute solution, eq 4.21 agrees with the result by Imai and Iwasa.[11] In the high-frequency limit, on the other hand, substituting $f_j = \partial\phi/\partial x = 0$ into eq C6 in Appendix C gives $U(\infty)$ as

$$U(\infty) = -V \sum_j z_j q n_j / \zeta_P \quad (4.22)$$

Equations 4.21 and 4.22 for the polyion mobility in the low- and high-frequency limits are in good agreement with the results from the qualitative estimation in section 2. This indicates that our picture for the polyion movement mentioned in section 2 is supported by the quantitative calculation.

5. Relation between ϵ^* and χ^*

Equation 4.12 is rewritten into the form

$$i\omega(\zeta\epsilon_0/zq)\chi^* + zqn_F(1 + \chi^*/\epsilon_s) + [\zeta(n - n_F) + \zeta_P/V]U^* = 0 \quad (5.1)$$

by using eqs 4.15–4.17 for the dilute solution without added salts and assuming again that the electrophoretic effect is negligible. By combining eqs 1.1, 4.14, and 5.1 in order to cancel σ^* and U^*, we obtain the relation between ϵ^* and χ^* as

$$\epsilon^* = \epsilon_s + \frac{\zeta_P + \zeta n V}{\zeta_P + \zeta(n - n_F)V} \left[\chi^* + \frac{z^2 q^2 n_F(\chi^* - \chi(0)]}{i\omega\epsilon_0\epsilon_s\zeta} \right] \quad (5.2)$$

and correspondingly $\sigma(0)$ as

$$\sigma(0) = \frac{z^2 q^2 n_F(\zeta_P + \zeta n V)}{\zeta[\zeta_P + \zeta(n - n_F)V]} \left(1 + \frac{\chi(0)}{\epsilon_s} \right) \quad (5.3)$$

Since ϵ^* has been related to χ^* as

$$\epsilon^* = \epsilon_s + \chi^* \quad (5.4)$$

in the conventional treatment based on the dipole moment formalism, eq 5.2 indicates a definite difference between the present treatment and the conventional one.

The dielectric increment $\Delta\epsilon$, defined by the difference between the low- and high-frequency limits of ϵ^*, is expressed from eq 5.2 as

$$\Delta\epsilon = \frac{\zeta_P + \zeta n V}{\zeta_P + \zeta(n - n_F)V} \left(\chi(0) + \frac{z^2 q^2 n_F \chi_1}{\epsilon_0\epsilon_s\zeta} \right) \quad (5.5)$$

where χ_1 is the coefficient of the first-order term in the power series of χ^* with respect to $i\omega$ as

$$\chi^* = \chi(0) + i\omega\chi_1 + O[(i\omega)^2] \quad (5.6)$$

As shown in Appendix D, on the other hand, a reciprocal

$\langle \tau^{-1} \rangle$ of the averaged relaxation time, defined from the retardation spectrum $L(\tau)$ by

$$\langle \tau^{-1} \rangle = \int_{-\infty}^{+\infty} \tau^{-1} L(\tau)\, \mathrm{d} \ln \tau \Big/ \int_{-\infty}^{+\infty} L(\tau)\, \mathrm{d} \ln \tau \quad (5.7)$$

is estimated as

$$\langle \tau^{-1} \rangle = \Delta\sigma / (\epsilon_0 \Delta\epsilon) \quad (5.8)$$

Here, $\Delta\sigma$ represents the conductivity increment, which is the difference between the low-frequency limit $\sigma(0)$ and the high-frequency limit $\sigma(\infty)$ of the real part of σ^*. From eqs 4.14 and 4.22, $\sigma(\infty)$ is given as

$$\sigma(\infty) = z^2 q^2 n(\zeta^{-1} + \zeta n V/\zeta_{\mathrm{P}}) \quad (5.9)$$

In the dilute solution where the second term in the parentheses of eq 5.3 is negligibly small compared with the first ones, $\Delta\sigma$ is given by

$$\Delta\sigma = z^2 q^2 (n - n_{\mathrm{F}}) \zeta \zeta_{\mathrm{P}} (\zeta^{-1} + nV/\zeta_{\mathrm{P}})^2 / [\zeta_{\mathrm{P}} + \zeta(n - n_{\mathrm{F}})V] \quad (5.10)$$

When the second term in the parentheses of eq 5.5 is also neglected, the substitution of eqs 5.5 and 5.10 into eq 5.8 gives the simple relation between $\langle \tau^{-1} \rangle$ and $\chi(0)$ as

$$\langle \tau^{-1} \rangle = z^2 q^2 (n - n_{\mathrm{F}})(\zeta^{-1} + nV/\zeta_{\mathrm{P}}) / [\epsilon_0 \chi(0)] \quad (5.11)$$

Equations 5.5 and 5.11 indicate that both $\Delta\epsilon$ and τ are influenced by ζ_{P}.

6. Application to Some Specific Cases

A. Dielectric Relaxation in Spherical Polyelectrolyte Solutions. Many theories reported so far[3] on the dielectric relaxation in a spherical polyelectrolyte solution, including the theory based on the conductivity formalism,[9] commonly treated the problem in the limit of excessive salts. In such a salt circumstance, U^* does not contribute explicitly to σ^* as suggested in eq 4.19, even if the mobility of the polyion is taken into account. In the present paper, we have treated the dielectric relaxation in the polyelectrolyte solution without added salts, which indicates the definite contribution of the polyion mobility to σ^* or ϵ^*.

The results in the present theory have been derived from the assumption that the dielectric constant is uniform over the whole cell. Most of the spherical polyions, however, have a different dielectric constant from the solvent. Hence, a minor modification that the dielectric constant inside the polyion is different from the outside is required in order to apply the present model to the spherical polyelectrolyte solution. As mentioned in Appendix E, the result (E8) is slightly different from eq 4.13 but still shows a close relation between σ^* and U^* in spherical polyelectrolyte solutions.

B. HF Dielectric Relaxation in Linear Polyelectrolyte Solutions. As mentioned in the Introduction, the HF dielectric relaxation in the semidilute region of the linear polyelectrolyte solution without added salts is ascribed to the movement of the loosely bound counterions in the direction perpendicular to the polyion axis within the range of the interpolyion distance (correlation length) ξ. The electric potential, in which the loosely bound counterions fluctuate, has a depth of the order of kT, owing to the shielding effect of the tightly bound counterions on the polyion charges, and is characterized by the two-dimensional quasi-periodicity of ξ. Taking into account the difference in the dimensionality, we can apply the present theory to this system simply by neglecting the z-axis.

The loosely bound counterions would exert little electrophoretic effect on U^* since, in the solution without added salts, they are more distant from the polyion than the tightly bound counterions, which implies that the assumption of free draining is valid. The proportional relation (4.14) between σ^* and U^* is thus applicable to the HF relaxation if n is replaced with $n_{\mathrm{L}} + n_{\mathrm{F}}$, where n_{L} is the number concentration of the loosely bound counterions. Furthermore, eqs 4.20 and 5.2 are also satisfied in the HF relaxation owing to the negligibly small size of the polyion compared with the cell size. As a consequence, the present model applies well to the HF relaxation of the linear polyelectrolyte solution. The HF dielectric relaxation measurements in the semidilute polyelectrolyte solutions are expected to give us information on the polyion mobility in the direction perpendicular to the long axis.

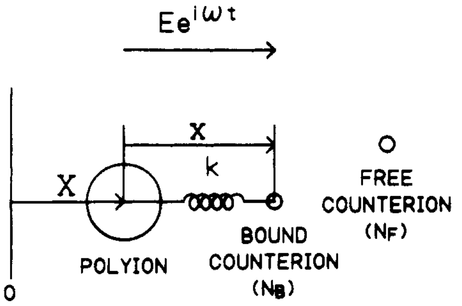

Figure 5. Spring model where the counterions are bound to the polyion by an effective spring with the force constant k.

C. LF Dielectric Relaxation in Linear Polyelectrolyte Solutions. The LF dielectric relaxation in linear polyelectrolyte solutions is ascribed to the movement of the tightly bound counterions along the long axis of a polyion. Recent experimental results[7] indicate that there exists a frictional force between the polyion and the tightly bound counterions, which arises from an undulating Coulombic potential along the long axis produced by the dissociated groups on the polyion. The frictional force of this type requires that the present model be modified for a quantitative discussion. This problem will be treated in a forthcoming paper.

Summary

The effect of polyion mobility on σ^* in polyelectrolyte solutions has been theoretically treated by using the conductivity formalism in the present paper. The qualitative consideration leads us to a close relation among the relaxations in U^*, σ^*, and ϵ^*, since they commonly arise from the competition between the frictional and Coulombic attractive forces, which have different frequency dependences. This conclusion is confirmed by quantitative calculations based on the cell model, which show that σ^* is proportional to U^* in the polyelectrolyte solution without added salts. Furthermore, the present treatment gives us the relation between ϵ^* and χ^* different from a conventional one. The present theory shows the significance of polyion mobility in the dielectric relaxation, particularly in the polyelectrolyte solution without added salts.

Appendix A: Spring Model

Let each of N_{B} bound counterions with the charge q and the friction constant ζ be bound to a polyion with charge $-Q$ and friction constant ζ_{P} by an effective spring with force constant k, as shown in Figure 5. Here, $X = W^* E e^{i\omega t}$ and $X + x = (W^* + w^*) E e^{i\omega t}$ are the displacements of the polyion and the bound counterions, respectively, from the origin of the coordinate and N_{F} is the number of free counterions per polyion. The electroneutrality gives us the relation between the charges of the polyion and counterions as $Q = (N_B + N_F)q$. In this case, the equations of motion for the polyion and the bound counterions are expressed as

$$i\omega\zeta_P W^* - kN_B w^* = -Q \tag{A1}$$

$$i\omega\zeta(w^* + W^*) + kw^* = q \tag{A2}$$

These simultaneous equations are easily solved as

$$W^* = -N_F q/[i\omega(\zeta_P + N_B\zeta)] - N_B\zeta(q\zeta_P + Q\zeta)/[k(\zeta_P + N_B\zeta)^2(1 + i\omega\tau)] \tag{A3}$$

$$w^* = (q\zeta_P + Q\zeta)/[k(\zeta_P + N_B\zeta)(1 + i\omega\tau)] \tag{A4}$$

where τ is the relaxation time defined by

$$\tau^{-1} = k(\zeta^{-1} + N_B/\zeta_P) \tag{A5}$$

On the other hand, the complex conductivity σ^* for the present model is given by

$$\sigma^* = i\omega\epsilon_s\epsilon_0 + i\omega[N_B q(w^* + W^*) - QW^*]/V + N_F q^2/(\zeta V) \tag{A6}$$

where the last term of the right-hand side is the contribution of the free counterions and V represents the solution volume per polyion. By using eqs A1 and A2, eq A6 reduces to

$$\begin{aligned}\sigma^* &= i\omega\epsilon_s\epsilon_0 - i\omega(Q + q\zeta_P/\zeta)W^*/V \\ &= i\omega\epsilon_s\epsilon_0 - (Q + q\zeta_P/\zeta)U^*/V\end{aligned} \tag{A7}$$

since $i\omega W^*$ is equal to the polyion mobility U^*. By substituting eq A3 into eq A7 and comparing it with eq 1.1, the dc conductivity $\sigma(0)$ and the dielectric increment $\Delta\epsilon$, defined by the difference between the low- and high-frequency limits of ϵ^*, are given by

$$\sigma(0) = N_F q(q\zeta_P + Q\zeta)/[\zeta(\zeta_P + N_B\zeta)V] \tag{A8}$$

$$\Delta\epsilon = N_B(q\zeta_P + Q\zeta)^2/[\epsilon_0 k(\zeta_P + N_B\zeta)^2 V] \tag{A9}$$

respectively. The electrical susceptibility χ^* due to the distortion of the bound counterion distribution is defined by

$$\chi^* = N_B q x/(\epsilon_0 V) \tag{A10}$$

By substituting eq A4 into eq A10, we have

$$\chi^* = N_B q(q\zeta_P + Q\zeta)/[\epsilon_0 k(\zeta_P + N_B\zeta)(1 + i\omega\tau)V] \tag{A11}$$

which reduces to

$$\chi(0) = N_B q(q\zeta_P + Q\zeta)/[\epsilon_0 k(\zeta_P + N_B\zeta)V] \tag{A12}$$

in the low-frequency limit. From eqs A9 and A12, we obtain the relation (5.5) between $\Delta\epsilon$ and $\chi(0)$ when the second term in the parenthesis of (5.5) is neglected. Furthermore, combining eq A12 with eq A5 gives us the relation (5.11) between τ and $\chi(0)$.

If the polyion is regarded as immobile (i.e., $\zeta_P \gg Q\zeta/q > N_B\zeta$), τ^{-1} in eq A5 is rewritten as $\tau^{-1} = k\zeta^{-1}$, and $\Delta\epsilon$ in eq A9 and $\chi(0)$ in eq A12 commonly reduce to $N_B q^2/(\epsilon_0 k V)$. These expressions for τ and $\Delta\epsilon$ (or $\chi(0)$) agree with those obtained from a simple spring model in which one end with the charge q and the friction constant ζ is connected to the other fixed end by a spring with the force constant k. Then, eqs A5, A9, and A12 involve the effect of the polyion mobility on τ, $\Delta\epsilon$, and $\chi(0)$; that is, the movement of the polyion reduces τ, increases $\Delta\epsilon$ and $\chi(0)$, and produces the difference between $\Delta\epsilon$ and $\chi(0)$.

Appendix B: Electrophoretic Effect on U^*

In this appendix, we consider in a qualitative manner the electrophoretic effect on U^*, particularly to see whether $U(\infty)$ remains larger than $U(0)$ even if the effect is taken into account. It is widely known that the polyion mobility (electrophoretic mobility) U^* is determined by the balance between the Coulombic and frictional forces acting on the polyion.[13] The Coulombic one is a sum of the external electric force F_{ep} and the force F_{cp} due to the distortion of the electric potential. The force F_{cp}, which is a reaction of the Coulombic attractive force F_{cb} exerted on the small ions, acts on the polyion in the opposite direction to F_{ep} and hence reduces U^* as shown in Figure 1a. Thus, we call F_{cp} the Coulombic retardation.

The frictional force, on the other hand, results from the Stokes friction on the polyion and the electrophoretic effect due to the frictional force F_{fb} exerted on the small ions. The electrophoretic effect means that the force $\mathbf{F}_s$ acting on the solvent, which is a reaction of F_{fb}, modifies the solvent flow and results in altering the frictional force on the polyion. This deformation of the solvent flow is expressed by the linearized Navier–Stokes equation

$$\eta\nabla^2\mathbf{u}_s E e^{i\omega t} - \operatorname{grad} P = -\sum_j \mathbf{F}_s F_{j0} \tag{B1}$$

where the right-hand side represents the external force acting on the solvent, which cancels out the frictional force F_{fb} exerted on the small ions. In eq B1, η is the viscosity coefficient of the solvent, P is the pressure in the solvent, and the inertial and time-derivative terms are neglected. Since the left-hand side of eq 3.8 represents F_{fb}, the substitution of eq 3.8 into eq B1 yields

$$\eta\nabla^2\mathbf{u}_s E e^{i\omega t} - \operatorname{grad} P = \sum_j z_j q F_{j0} \operatorname{grad} x E e^{i\omega t} - \sum_j F_{j0} \operatorname{grad} \psi_j \tag{B2}$$

Although the right-hand side in eq B2 includes the contribution of all the small ions, the small ions near the polyion, that is, the bound counterions, should contribute mainly to the electrophoretic effect. Then, we will take into account $\mathbf{F}_s$ arising from the bound counterions alone in the following qualitative consideration.

The first term of the right-hand side in eq B2 represents the force F_{es} acting on the solvent, which is equal to the external electric force F_{eb} exerted on the bound counterions. Thus, the force F_{es} is in the opposite direction to the polyion movement, that is, in the same direction as the solvent flow, and hence increases the drag exerted on the polyion. As a consequence, the first term of the right-hand side in eq B2 reduces U^*, which is thus called the electrophoretic retardation.[13] Since eq B2 indicates that F_{es} is independent of the frequency ω apart from the factor $e^{i\omega t}$, the electrophoretic retardation is independent of ω and has no influence on the frequency dependence of U^*.

The second term of the right-hand side in eq B2 arises from the distortions of the small ion distribution and the electric potential and represents the Coulombic attractive force F_{cb} acting on the bound counterions from the polyion. As mentioned in section 2, F_{cb} is the largest in the low-frequency limit, decreases with increasing ω, and vanishes in the high-frequency limit. Since F_{cb} acts on the solvent in the opposite direction to F_{eb} as shown in Figure 1a, F_{cb} decreases the electrophoretic retardation due to F_{eb}, which we call the electrophoretic acceleration. On the other hand, the force F_{cp} exerted on the polyion, a reaction of F_{cb}, produces the Coulombic retardation, which reduces U^* as mentioned above. The Coulombic

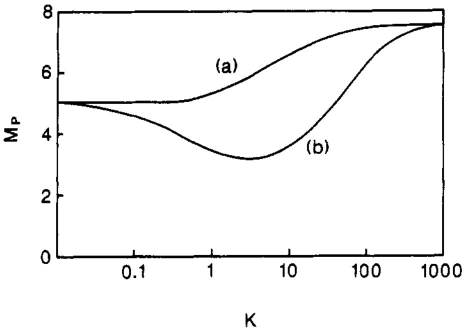

Figure 6. Plot of the reduced electrophoretic mobility $M_P = 6\pi\eta q U(0)/(\epsilon_0\epsilon_s kT)$ against $K = \kappa a$ from Figure 4 in ref 13 where η is the viscosity coefficient, κ^{-1} the Debye length, and a the polyion radius. The parameter values used are the reduced surface potential $q\Phi_0/kT = 5$ on the spherical particle, $z_1 = -z_2 = 1$, $\zeta_1 = \zeta_2 = 3.66 \times 10^{-36}$ J s m^{-2}.

retardation arising from F_{cp} affects U^* directly, while the electrophoretic accereleration due to F_{cp} exerts only indirect influence on U^* through the solvent as medium. Then, the net effect due to the Coulombic attractive force between the polyion and the bound counterions reduces U^*. Since the Coulombic attractive force vanishes in the high-frequency limit, the polyion mobility $U(\infty)$ in the high-frequency limit should be larger than $U(0)$ in the low-frequency limit, even if the electrophoretic effect is taken into account.

This qualitative conclusion is supported by the quantitative calculation in the case of the spherical polyion. Wiersema et al.[13] calculated the electrophoretic mobility $U(0)$ of a spherical charged particle in the limit of excessive salts. They obtained curve a in Figure 6 as a first approximation by omitting the distortion ψ_j given as eq 3.9 in the fundamental equations (3.1)–(3.3) and (B2) and then calculated curve b by taking into account the distortion through successive approximations. As a result, curves a and b can be regarded as $U(\infty)$ and $U(0)$, respectively, in our treatment. Figure 6 shows that $U(\infty)$ is larger than $U(0)$ for any ionic strength, which supports the qualitative conclusion on the frequency dependence of U^* in this appendix and section 2.

Appendix C: Derivation of Equation 4.10

The volume integral of the right-hand side in the Poisson equation (3.3) multiplied by $\partial\Phi/\partial x$ over the cell is given by

$$\int \frac{\partial \Phi}{\partial x}\nabla^2\Phi \, \mathrm{d}V = \int \frac{\partial \Phi}{\partial x} \mathrm{grad}_n \, \Phi \, \mathrm{d}S - \frac{1}{2}\int \frac{\partial}{\partial x}|\mathrm{grad}\, \Phi|^2 \, \mathrm{d}V = \int \frac{\partial \Phi}{\partial x} \mathrm{grad}_n \, \Phi \, \mathrm{d}S - \frac{1}{2}[\int_{S_{+x}} |\mathrm{grad}\, \Phi|^2 \, \mathrm{d}S - \int_{S_{-x}} |\mathrm{grad}\, \Phi|^2 \, \mathrm{d}S] \quad \text{(C1)}$$

The first term of the right-hand side in eq C1 vanishes from the boundary conditions (3.10) and (3.11) as

$$\int \frac{\partial \Phi}{\partial x} \mathrm{grad}_n \, \Phi \, \mathrm{d}S = \int_{S_{+x}} \left(\frac{\partial \Phi}{\partial x}\right)^2 \mathrm{d}S - \int_{S_{-x}} \left(\frac{\partial \Phi}{\partial x}\right)^2 \mathrm{d}S = 0 \quad \text{(C2)}$$

Furthermore, the boundary condition (3.12) indicates that the terms in the bracket of eq C1 become equal to eq C2 and hence also reduce to zero. As a consequence, we obtain the relation[11]

$$\int \frac{\partial \Phi}{\partial x}\nabla^2\Phi \, \mathrm{d}V = 0 \quad \text{(C3)}$$

By substituting eq 3.3 into eq C3, we obtain

$$\sum_j z_j q \int \frac{\partial \Phi}{\partial x} F_j \, \mathrm{d}V + q \int \frac{\partial \Phi}{\partial x} F_P \, \mathrm{d}V = 0 \quad \text{(C4)}$$

or

$$\sum_j z_{jq} \int \frac{\partial(\Phi_0 + \phi E e^{i\omega t})}{\partial x} F_j \, \mathrm{d}V + q \int \frac{\partial(\Phi_0 + \phi E e^{i\omega t})}{\partial x} F_P \, \mathrm{d}V = 0 \quad \text{(C5)}$$

where the first and second terms on the left-hand side of eq C5 represent the Coulombic attractive forces in the x-direction, which are exerted on the small ions and the polyion, respectively. Thus, eq C5 indicates the law of action and reaction in the Coulombic attraction. Since the Coulombic force exerted on the polyion including the external force cancels out the frictional force on the polyion, eq C4 results in the form

$$\sum_j z_j q \int \frac{\partial \Phi}{\partial x} F_j \, \mathrm{d}V - \zeta_P U^* E e^{i\omega t} = 0 \quad \text{(C6)}$$

If the both sides of eq 3.2 are multiplied by F_j, we obtain

$$z_j q \frac{\partial \Phi}{\partial x} F_j = -kT \frac{\partial F_j}{\partial x} - \zeta_j (u_{jx} - u_{sx}) F_j E e^{i\omega t} \quad \text{(C7)}$$

By integrating the both sides of eq C7 over the cell, we have

$$\sum_j z_j q \int \frac{\partial \Phi}{\partial x} F_j \, \mathrm{d}V = -\sum_j \zeta_j \int (u_{jx} - u_{sx}) F_j E e^{i\omega t} \, \mathrm{d}V \quad \text{(C8)}$$

since the first term of the right-hand side vanishes owing to the boundary condition (3.13). Equation C8 indicates that the total of the Coulombic force exerted on the small ions cancels out the total of the frictional force on the small ions over the cell since the total of the diffusional force vanishes from the boundary condition (3.13). The substitution of eq C8 into eq C6 yields the relation

$$\sum_j \zeta_j \int (u_{jx} - u_{sx}) F_j \, \mathrm{d}V + \zeta_P U^* = 0 \quad \text{(C9)}$$

which can be regarded as a law of action and reaction in the frictional forces through the solvent as medium.

Appendix D: $i\omega$ and $(i\omega)^{-1}$ Expansions of σ^*

In the low-frequency limit, the complex conductivity σ^* is expanded in a power series with respect to $i\omega$ as

$$\sigma^* = \sum_{k=0}^{\infty} (i\omega)^k a_k \quad \text{(D1)}$$

By combining eq D1 with eq 1.1, we get

$$a_0 = \sigma(0) \quad \text{(D2)}$$

In a dielectric relaxation with the multiple relaxation time τ, on the other hand, the complex dielectric constant is expressed by using the retardation spectrum $L(\tau)$ as

$$\epsilon^* = \epsilon(\infty) + \int_{-\infty}^{+\infty} \frac{L(\tau)}{1 + i\omega\tau} \, \mathrm{d} \ln \tau \quad \text{(D3)}$$

By substituting eq D3 expanded in a power series of $i\omega$ into eq 1.1 and comparing it with eq D1, we have

$$a_1 = \epsilon_0 \epsilon(0) = \epsilon_0[\Delta\epsilon + \epsilon(\infty)] \quad \text{(D4)}$$

$$a_k = (-1)^{k-1}\epsilon_0\Delta\epsilon\langle\tau^{k-1}\rangle \qquad (k \geq 2) \tag{D5}$$

where $\epsilon(0)$ is the low-frequency limit of ϵ^*, $\Delta\epsilon$ represents the dielectric increment defined by

$$\Delta\epsilon = \int_{-\infty}^{+\infty} L(\tau)\,\mathrm{d}\ln\tau \tag{D6}$$

and $\langle(...)\rangle$ indicates the average with respect to $L(\tau)$ as

$$\langle(...)\rangle = \int_{-\infty}^{+\infty}(...)L(\tau)\,\mathrm{d}\ln\tau \Big/ \int_{-\infty}^{+\infty}L(\tau)\,\mathrm{d}\ln\tau \tag{D7}$$

In the high-frequency limit, σ^* is similarly expanded in a power series of $(i\omega)^{-1}$ as

$$\sigma^* = \sum_{k=-1}^{\infty}(i\omega)^{-k}b_k \tag{D8}$$

By substituting eq D3 expanded in a power series of $(i\omega)^{-1}$ into eq 1.1 and comparing it with eq D8, we obtain

$$b_{-1} = \epsilon_0\epsilon(\infty) \tag{D9}$$

$$b_0 = \sigma(\infty) = \sigma(0) + \epsilon_0\Delta\epsilon\langle\tau^{-1}\rangle \tag{D10}$$

$$b_k = (-1)^k\epsilon_0\Delta\epsilon\langle\tau^{-k-1}\rangle \qquad (k \geq 1) \tag{D11}$$

where $\sigma(\infty)$ is the high-frequency limit of the real part of σ^*. From eqs D4 and D9, $\Delta\epsilon$ is expressed as

$$\epsilon_0\Delta\epsilon = a_1 - b_{-1} \tag{D12}$$

By combining eq D5 with eq D10, a reciprocal $\langle\tau^{-1}\rangle$ of the averaged relaxation time is given by

$$\langle\tau^{-1}\rangle = \Delta\sigma/(\epsilon_0\Delta\epsilon) = (b_0 - a_0)/(a_1 - b_{-1}) \tag{D13}$$

where $\Delta\sigma$ represents the conductivity increment defined by the difference between the low- and high-frequency limits of the real part of σ^*. By the $i\omega$ or $(i\omega)^{-1}$ expansion of the distribution and the electric potential, the significant parameters $\Delta\sigma$ and $\Delta\epsilon$ in the dielectric relaxation can be estimated easily compared with the frequency-dependent σ^* or ϵ^*. In this case, we can also evaluate the average relaxation time $\langle\tau^{-1}\rangle^{-1}$ from eq D13.

Appendix E: Spherical Polyion with a Different Dielectric Constant from the Solvent

We suppose that a spherical polyion with the radius a and the dielectric constant ϵ_P has the dissociated groups on the outer surface. The electric potentials Φ, Φ_0, and ϕ for the outside of the polyion, which appear in sections 3 and 4 and Appendix C, are replaced with Φ_{out}, $\Phi_{0,\mathrm{out}}$, and ϕ_{out}, respectively, in this appendix. The electric potential Φ_{in} inside the polyion satisfies the following Poisson equation

$$\nabla^2\Phi_{\mathrm{in}} = 0 \tag{E1}$$

If a is much smaller than L, Φ_{in} induced by the external electric field $Ee^{i\omega t}$ is hardly affected by the cubic boundary and hence can be written as

$$\Phi_{\mathrm{in}} = \Phi_{0,\mathrm{in}} + (\phi_{\mathrm{in}} - 1)r\cos\theta\, Ee^{i\omega t} \tag{E2}$$

where $\Phi_{0,\mathrm{in}}$ and ϕ_{in} are constants and θ is the angle between the radius vector $\mathbf{r}$ of the polyion and the x-axis. The boundary condition of the electric potential on the surface S_{in} ($r \equiv |\mathbf{r}| = a$) of the polyion sphere is given by

$$\epsilon_P\frac{\partial\Phi_{\mathrm{in}}}{\partial r} = \epsilon_s\frac{\partial\Phi_{\mathrm{out}}}{\partial r}, \qquad \frac{\partial\Phi_{\mathrm{in}}}{\partial\theta} = \frac{\partial\Phi_{\mathrm{out}}}{\partial\theta} \tag{E3}$$

where ϵ_s is the dielectric constant of the solvent.

In the present case, eq 4.5 is rewritten as

$$\sigma^* = \sum_j z_j q\int F_{j0}u_{jx}\,\mathrm{d}V/V + i\omega\epsilon_0(\epsilon_s + \chi_P^*) \tag{E4}$$

where the susceptibility χ_P^* is obtained from the boundary condition (E3) as

$$\chi_P^* = (4\pi a^3/3)(\epsilon_s - \epsilon_P)(\phi_{\mathrm{in}} - 1)/V \tag{E5}$$

As mentioned in Appendix C, the surface integrals on the cubic cell derived from the volume integral $\int(\partial\Phi_{\mathrm{out}}/\partial x)\nabla^2\Phi_{\mathrm{out}}\,\mathrm{d}V_{\mathrm{out}}$ become zero from the boundary conditions (3.10)–(3.13), (E3), and (E2), where $\mathrm{d}V_{\mathrm{out}}$ represents the volume element of the region outside the sphere. Thus, eqs C4–C6 are valid for this model if Φ and $\mathrm{d}V$ are replaced with Φ_{out} and $\mathrm{d}V_{\mathrm{out}}$, respectively. The relation (C8), on the other hand, is rewritten for this model as

$$\sum_j z_j q\int\frac{\partial\Phi_{\mathrm{out}}}{\partial x}F_j\,\mathrm{d}V_{\mathrm{out}} = \Big[\delta^* - \sum_j\zeta_j\int(u_{jx} - u_{sx})F_j\,\mathrm{d}V_{\mathrm{out}}\Big]Ee^{i\omega t} \tag{E6}$$

where δ^* is defined by $\delta^* = kT\int F_{j0}f_j\cos\theta\,\mathrm{d}S_{\mathrm{in}}$ and represents the distortion of the small ion distribution on the sphere surface. By using eq E6, eq C9 is modified as

$$\sum_j\zeta_j\int(u_{jx} - u_{sx})F_j\,\mathrm{d}V + \zeta_P U^* - \delta^* = 0 \tag{E7}$$

Assuming that the electrophoretic effect is negligible in the polyelectrolyte solution without added salts, σ^* is derived from eqs E4 and E7 as

$$\sigma^* = i\omega\epsilon_0(\epsilon_s + \chi_P^*) + (zq/\zeta V)\Big[\zeta\int F_0u_{sx}\,\mathrm{d}V_{\mathrm{out}} - \zeta_P U^* - \delta^*\Big] \tag{E8}$$

by using similar calculations to those in section 4.

References and Notes

(1) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(2) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
(3) Mandel, M.; Odijk, T. *Annu. Rev. Phys. Chem.* **1984**, *35*, 75.
(4) Minakata, A.; Imai, N. *Biopolymers* **1972**, *11*, 347.
(5) van der Touw, F.; Mandel, M. *Biophys. Chem.* **1974**, *2*, 218, 231.
(6) Ito, K.; Yagi, A.; Ookubo, N.; Hayakawa, R. *Macromolecules* **1990**, *23*, 857.
(7) Ookubo, N.; Hirai, Y.; Ito, K.; Hayakawa, R. *Macromolecules* **1989**, *22*, 1359.
(8) Chew, W. C.; Sen, P. N. *J. Chem. Phys.* **1982**, *77*, 4683.
(9) DeLacy, E. H. B.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 2007.
(10) Kwak, J. C. T.; Hayes, R. C. *J. Phys. Chem.* **1975**, *79*, 265.
(11) Imai, N.; Iwasa, K. *Isr. J. Chem.* **1972**, *11*, 223.
(12) Schmitz, K. S. *J. Chem. Phys.* **1983**, *79*, 4029.
(13) Wiersema, P. H.; Loeb, A. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1966**, *22*, 78.