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DIELECTRIC INCREMENT IN POLYION SOLUTIONS DUE TO THE DISTORTION OF COUNTERION DISTRIBUTION

Nobuhisa IMAI and Shigeo SASAKI
Department of Physics, Faculty of Science, Nagoya University, Nagoya 464, Japan

A theory of DC dielectric increment, $\delta\epsilon$, has been constructed based on the Fokker–Planck and Poisson equations on the mechanism of the distortion of spatial counterion distribution around a rodlike polyion under the applied electric field, E, perpendicular to the polyion rod. The DC dielectric constant of polyion solutions can be obtained analytically in the both cases of absence and presence of counterion-flow. The nonlinearity of the Poisson–Boltzmann equation in the absence of E has given the interesting behaviors of $\delta\epsilon$. The calculation in the absence of counterion-flow has shown the $\delta\epsilon$-values having the same order of magnitude as the experimental data at the higher frequency range (around 100 kHz), and the importance of this mechanism has been pointed out.

1. Introduction

The characteristic properties of dielectric constant of linear polyelectrolyte solutions are briefly summarized as the tremendous dielectric increment at extremely low frequency and the very broad dispersion pattern roughly composed of a few relaxation processes in the wide frequency range. These properties have been theoretically clarified as due to the replacement of the highly condensed counterions around a macroion. The roles of the counterions discussed in the theories may be classified simply into the following mechanisms [1–15];

(1) the Maxwell–Wagner effect based on the multiphase model

(2) the effect of the surface conductivity due to the counterion migration on macroion surface

(3) the effect of the displacement or the fluctuation of counterions (through the potential barrier) along the polyion rod.

Each of these effects represents the character of the counterions bound to the polyion on the different standpoints.

However, no theoretical studies have been done on the dipolemoment due to the distortion of the spatial distribution of counterions around polyions under the applied electric field. It is of interest to construct the theory on the basis of irreversible statistical thermodynamics for the counterions without introducing the assumption of discrete phase models or the concept of phenomenological conductances.

In this paper, we develop a theory of DC dielectric constant of polyion solutions based on a model of continuous spatial distribution of counterions by using Fokker–Planck and Poisson equations. This treatment is generally accompanied by a considerable mathematical difficulty even under the assumption of sufficiently low applied electric field E, because of the presence of an original complicated electric potential around polyion in the absence of E due to the non-linear character of the Poisson–Boltzmann equation. Therefore, our present study restricts the object to the system satisfying the following conditions; the system is two dimensional, that is, polyions have a rodlike shape whose axis is perpendicular to the outer applied electric field, the polyion solution is salt-free, and only coulombic interaction exists between the polyion and the counterions. Here, we study the DC dielectric increment in the cases of the absence and the presence of counterion-flow.

It has been concluded through our present derivation that the expression of DC dielectric increment can be analytically obtainable in the two-dimensional system even in the case of the presence of counterion flow, and that the dielectric increment due to the dipolemoment resulting from the distortion of counterion atmosphere on the plane perpendicular to the polyion-

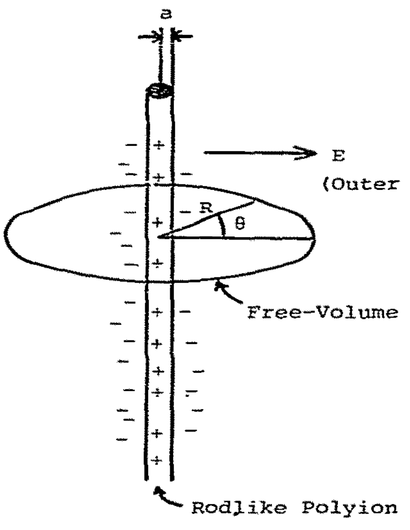

Fig. 1. Counterions and applied electric field perpendicular to rodlike polyion.

axis is as large as experimental values observed at the higher frequency side. It has been also demonstrated that the counterion-flow considerably decreases the amount of the dipolemoment resulting from the distortion of counterion distribution.

2. Model and fundamental equations

The axis of the polyion rod is assumed to be oriented perpendicular to the external electric field. (see fig. 1.) This electric field should bring about the distortion of the spatial distribution of the counterions from their thermal equilibrium.

Let us assume that a polyion rod of radius a is situated in its coaxial cylindrical free-volume of radius R. In the absence of E, the counterion distribution has been obtained from the Poisson–Boltzmann equation [16,17]. In the presence of E, the distribution function of counterions, f_c, can be described by the following Fokker–Planck and Poisson equations,

$$\partial f_c/\partial t = D_f \nabla \cdot \{\nabla + \nabla\phi\} f_c \,, \tag{2.1}$$

$$\nabla^2 \phi = -(4\pi e_0^2/\epsilon_0 kT) f_c \,, \tag{2.2}$$

where ϕ, D_f and ϵ_0 are the reduced electric potential (defined by the electric potential multiplied by e_0/kT), the diffusion constant of counterion, and the dielectric constant of the medium, respectively. The potential, ϕ, is composed of the two terms, the standard potential ϕ_0 in the absence of E, and the potential deviation ϕ_1 in the presence of E.

On the free-volume surface it is reasonable to put

$$\phi_1(R,\theta) = -(e_0/kT)ER\cos\theta \,, \tag{2.3}$$

concerning the overall applied electric field E. Under very low external field E, the θ-dependence of ϕ_1 should be the same as eq. (2.3), so that $\phi_1(r,\theta)$ and $\phi(r,\theta)$ may be given in the forms

$$\phi_1(r,\theta) = q(r)\cos\theta \,, \tag{2.4}$$

$$\phi = \phi_0(r) + q(r)\cos\theta \,, \tag{2.5}$$

where r and θ are cylinder coordinates. The equilibrium potential ϕ_0 satisfies the Poisson–Boltzmann equation;

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} r \frac{\mathrm{d}}{\mathrm{d}r}\phi_0 = -\kappa^2 e^{-\phi_0} \,, \tag{2.6}$$

where ϕ_0 is promissed to be zero at $r = R$ and κ is defined by

$$\kappa^2 = 4\pi e_0^2 a_- /kT \,. \tag{2.7}$$

Here the counterion is assumed to have the univalent negative charge and a_- is the number density of the counterion at $r = R$. The solution of the differential equation (2.6) has been given by

$$\phi_0 = \ln\{\kappa^2 r^2 \sinh^2(A\ln r + B)/2A^2\} \,, \tag{2.8}$$

where the integration constants A and B are determined under the conditions $\phi_0(R) = 0$ and $\mathrm{d}\phi_0/\mathrm{d}r|_{r=R} = 0$ as

$$A = \sqrt{1 - \tfrac{1}{2}\kappa^2 R^2} \,, \tag{2.9}$$

$$B = \ln\left(\frac{1-A}{1+A}\right) - A\ln R \,. \tag{2.10}$$

Let us split f_c in the same way as ϕ;

$$f_c = f_0(1 + u(r)\cos\theta) \,, \tag{2.11}$$

where f_0 is the Poisson–Boltzmann distribution, $f_0 \equiv a_- e^{-\phi_0}$, and $u(r)$ represents the degree of the distortion. Both $|u(r)|$ and $|q(r)|$ are much smaller than unity when E is very low, as our present case. Substituting eqs. (2.5) and (2.11) into eqs. (2.1) and (2.2), and neglecting higher power terms of u and q, we can rewrite eqs. (2.1) and (2.2) in the following forms

$$\frac{\partial}{\partial t} u = D_{\mathrm{f}} \nabla \cdot \{f_0 \nabla (u+q) \cos\theta\} , \tag{2.12}$$

or

$$\frac{\partial}{\partial t} u = D_{\mathrm{f}} \left\{ \frac{\partial^2}{\partial r^2} (u+q) + \left(\frac{1}{r} - \frac{\mathrm{d}\phi_0}{\mathrm{d}r} \right) \frac{\partial}{\partial r} (u+q) - \frac{1}{r^2} (u+q) \right\} , \tag{2.13}$$

and

$$\frac{\partial}{\partial r} \frac{1}{r} \frac{\partial}{\partial r} rq = -\kappa^2 \mathrm{e}^{-\phi_0} u . \tag{2.14}$$

The expression of ion-flux I_{f} is given from eq. (2.12) as

$$I_{\mathrm{f}} = D_{\mathrm{f}} f_0 \nabla J \cos\theta , \tag{2.15}$$

where J defined by

$$J \equiv u + q .$$

If E is a sinusoidal function of time whose angular frequency is ω, eq. (2.13) can be rewritten as

$$\mathrm{i}\underset{\sim}{\omega} u = \frac{\partial^2}{\partial r^2} J + \left(\frac{1}{r} - \frac{\mathrm{d}\phi_0}{\mathrm{d}r} \right) \frac{\partial}{\partial r} J - \frac{1}{r^2} J , \tag{2.16}$$

where $\underset{\sim}{\omega} = \omega / D_0$. Although it is very difficult to find the general solution of eq. (2.16), the equation when $\omega = 0$;

$$0 = \frac{\partial^2}{\partial r^2} J + \left(\frac{1}{r} - \frac{\mathrm{d}\phi_0}{\partial r} \right) \frac{\partial}{\partial r} J - \frac{1}{r^2} J , \tag{2.17}$$

can be analytically solved as shown in the next section. It can be easily shown that eq. (2.17) is available only if the condition $\omega R^2 \ll 1$ is satisfied from the fact that the right-hand side of eq. (2.17) has a value of order u/R^2.

Now, the dipolemoment μ induced by the distortion of counterion distribution can be expressed as

$$\mu = -2e_0 \int^{2\pi} \int_a^R f_0 u(r) r^2 \cos^2\theta \, \mathrm{d}r \, \mathrm{d}\theta . \tag{2.18}$$

Substituting eq. (2.14) into eq. (2.18), we have a convenient expression of μ;

$$\mu = -\frac{\epsilon_0 kT}{4e_0} [R q_{\mathrm{R}}^{(1)} - R q_{\mathrm{R}} - a^2 q_a^{(1)}] , \tag{2.19}$$

where $q_R \equiv q(R)$, $q_R^{(1)} = \partial q / \partial r|_{r=R}$ and $q_{\mathrm{a}}^{(1)} = \partial q / \partial r|_{r=a}$. For simplicity, in eq. (2.19) we have chosen the boundary condition for q such that electric potential on the polyion surface is not altered by E

$$q(a) = 0 . \tag{2.20}$$

As discussed in the last section, the boundary condition at $r = a$ was not essential for the final numerical values of dielectric increment $\delta\epsilon$. The expression for $\delta\epsilon$, in this system can be obtained from the general equation,

$$\delta\epsilon = -4\pi\mu / \pi R^2 E . \tag{2.21}$$

3. Integration of the equations

For simplicity hereafter we use the following notations. The functions, for instance, J, q, etc. at $r = R$ or $r = a$ will be denoted by suffix R or a as J_R, q_R, or J_a, q_a, and the first derivative with respect to r will be denoted by putting (1) on the shoulder of the function as $J^{(1)}$ or $q^{(1)}$. $J_{\mathrm{R}}^{(1)}$ means $\mathrm{d}J/\mathrm{d}r$ at $r = R$.

At first from eqs. (2.6), (2.14) and (2.17), we have the following relation,

$$\frac{\mathrm{d}}{\mathrm{d}r} \left(q + \frac{q}{r} \right) - \phi_0^{(1)} \left(q^{(1)} + \frac{q}{r} \right) + \kappa^2 r \mathrm{e}^{\phi_0} J^{(1)} = (1/r) \{ \kappa^2 R q_R + \kappa^2 R (R J_R^{(1)} - J_R) \} . \tag{3.1}$$

Integration of eq. (3.1) over whole free-volume leads the following relation;

$$q_R^{(1)} + q_R / R - q_a' \mathrm{e}^{\phi_0(a)} = \int_a^R \{ \kappa^2 R (q_R + R J_R^{(1)} - J_R) \mathrm{e}^{\phi_0} / r - \kappa^2 r J^{(1)} \} \, \mathrm{d}r . \tag{3.2}$$

Since the following relation is established between the polyion charge per length, ne_0, and $\phi_0^{(1)}(a)$;

$$(r \phi_0^{(1)})_a = 2ne_0^2 / DkT \equiv 2\lambda , \tag{3.3}$$

we obtain the relation

$$2q_a^{(1)} = \kappa^2 R q_R + \kappa^2 R (R J_R^{(1)} - J_R) - \kappa^2 a \mathrm{e}^{-\phi_0(a)} (a J_a^{(1)} - J_a) , \tag{3.4}$$

by putting $r = a$ in eq. (3.1). In deriving eq. (3.4), the relation obtained from eq. (2.14);

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(q^{(1)}+\frac{q}{r}\right)=-\kappa^2 \mathrm{e}^{-\phi_0}u ,$$

and the boundary condition (2.20) have been also taken into the consideration.

Substituting $q_a^{(1)}$-expression of eq. (3.4) into eq. (3.2) and performing the integration of e^{ϕ_0}/r in eq. (3.4), we can obtain from eq. (3.2) the direct expression of the right-hand side of eq. (2.19).

[cf: The integration of e^{ϕ_0}/r can be easily obtained from the relation;

$$\kappa^2R^2\mathrm{e}^{\phi_0}/r=\tfrac{1}{4}(\mathrm{d}/\mathrm{d}r)(\kappa^2r^2+8\mathrm{e}^{\phi_0}-2r\phi_0^{(1)}\mathrm{e}^{\phi_0}) ,$$

which is derived from eq. (2.6).]

Thus, $\delta\epsilon$ is expressed by the following equation.

$$\frac{\delta\epsilon}{D}=\tfrac{1}{4}\kappa^2(R^2-a^2)+\frac{RJ_R^{(1)}-J_R}{q_R}\left\{2+\frac{\kappa^2}{4}(R^2-a^2)\right\}$$
$$-\frac{\kappa^2R}{q_R}\int_a^R rJ^{(1)}\mathrm{d}r-\frac{a}{R}(2-\lambda)\frac{aJ_a^{(1)}-J_a^{(1)}}{q_R} . \qquad (3.5)$$

If we obtain κ^2 from eq. (2.6) and find the $J(r)$-expression from eq. (2.17), $\delta\epsilon$ can be obtained from the above formulae.

In order to solve eq. (2.17) with respect to $J(r)$, the following concrete expression of $\phi_0^{(1)}$, obtained from eq. (2.8), must be substituted into eq. (2.12);

$$r\phi_0^{(1)}=-2A\coth(A\ln r+B)-2 , \qquad (3.6)$$

where the direct relation between λ and A is given from eqs. (2.9), (2.10) and (3.3) as follows

$$1-\lambda=-A\left\{\frac{1-A+(a/R)^{-2A}}{1-A-(a/R)^{-2A}}\right\} . \qquad (3.7)$$

By introducing the following variable S instead of r;

$$S\equiv\frac{\coth(A\ln r+B)+1}{\coth(A\ln r+B)-1} \qquad (3.8)$$

eq. (2.17) is transformed into a simplified form;

$$S(1-S)\frac{\mathrm{d}^2J}{\mathrm{d}S^2}+\left(2-\frac{1}{A}+\frac{S}{A}\right)\frac{\mathrm{d}J}{\mathrm{d}S}-\frac{J(1-S)}{4A^2S}=0 . \qquad (3.9)$$

This equation can be solved and expressed with hypergeometric functions, that is, the two independent solutions of eq. (3.9), $J_1(S)$ and $J_2(S)$, are written as,

$$J_1(S)=S^lF(\alpha,\beta,\gamma;S) , \qquad (3.10)$$
$$J_2(S)=S^{-1-\gamma-l}F(\alpha-\gamma+1,\beta-\gamma+1,2-\gamma;S), \qquad (3.11)$$

where $F(\alpha,\beta,\gamma;S)$ represents the hyper geometric function whose parameters l,α,β and γ are defined with A by

$$l=(1/2A)(1-A)-h_-,\quad \alpha=h_+-h_--1 ,$$
$$\beta=-h_+-h_--1,\quad \gamma=1-2h_- , \qquad (3.12)$$

in which

$$h_+=\frac{1}{2A}(A^2+2A+2)^{1/2},\quad h_-=\frac{-1}{2A}(A^2-2A+2)^{1/2}.$$

The parameter A takes real values when $\kappa^2R^2<2$, but it changes to pure imaginary when $\kappa^2R^2>2$, as seen in eq. (2.9). For the real values of A, the expressions of eqs. (3.10) and (3.11) are valid in the convergence range for the given boundary conditions. For the imaginary A, however, the above J_1 and J_2 must take the following forms. [cf. The complex conjugates of the above J_1 and J_2 are also the solutions of eq. (3.9)]

$$J_1(S)=\mathrm{Re}\,[S^lF(\alpha,\beta,\gamma;S)] , \qquad (3.10)'$$
$$J_2(S)=\mathrm{Re}\,[S^{-1-\gamma-l}F(\alpha-\gamma+1,\beta-\gamma+1.2-\gamma:S)], \qquad (3.11)'$$

where Re means the real part.

The linear combination of J_1 and J_2, each multiplied by an arbitrary constant, gives the general expression of $J(r)$. These two constants are determined by the two boundary conditions at $r=R$ or a.

Here, the boundary conditions, $J_R=q_R$ (that is $u_R=0$) and $J_a=0$ (or $J_a^{(1)}=0$) are adopted for the case when the counterion-flow is present. *The former condition $u_R=0$ corresponds to the case when there is no macroscopic overall uneven distribution of counterions happening in the solution under the applied electric field, and the latter condition, $J_a=0$ means that there is no distortion of the ion density and also no ion-flow on the polyion surface.* (Another condition $J_a^{(1)}=0$ instead of $J_a=0$ means the non ion-flux in radial direction on the polyion surface.)

4. Calculations of $\delta\epsilon$

In our present work, $\delta\epsilon$ has been obtained for the following cases; one is the case of non ion-flow ($J=0$), and the other is the case of ion-flow under the conditions $u_R=0$ and $J_a=0$ (or $u_R=0$ and $J_a^{(1)}=0$).

4.1. The system without counterion flow ($J = 0$)

In this case we can obtain $\delta\epsilon$ from eq. (3.5) immediately by putting all the J-terms zero as follows;

$$\delta\epsilon/D = \tfrac{1}{4}\kappa^2(R^2 - a^2)\,, \tag{4.1}$$

or under the consideration of eq. (2.9)

$$\delta\epsilon/D = \tfrac{1}{2}(1 - A^2)(1 - a^2/R^2)\,. \tag{4.2}$$

Eq. (4.1) shows that the dielectric increment in the case of non ion-flow is proportional to counterion activity. The relation eq. (4.1) can be transformed into the following form by eqs. (2.8) and (3.7);

$$\frac{\delta\epsilon}{D} = 4\lambda(1 - \tfrac{1}{2})\,\frac{1 - (a^2/R^2)}{1 - e^{-\phi_0(a)}(a^2/R^2)}\,. \tag{4.3}$$

Thus, $\delta\epsilon$ can be obtained if $\phi_0(a)$ is given as a function of λ. Especially if polyion radius a is sufficiently small, $\delta\epsilon$ becomes simply:

$$\delta\epsilon/D = \lambda(2 - \lambda)/2\,. \tag{4.4}$$

On the basis of eq. (4.3) the numerical calculation was performed for various a/R as a function of charge parameter λ of polyion, and the results are shown in fig. 2, in which the dotted line represents the case $a \to 0$. The flat range of the lines for $\lambda \geqslant 1$ shows the ion-condensation.

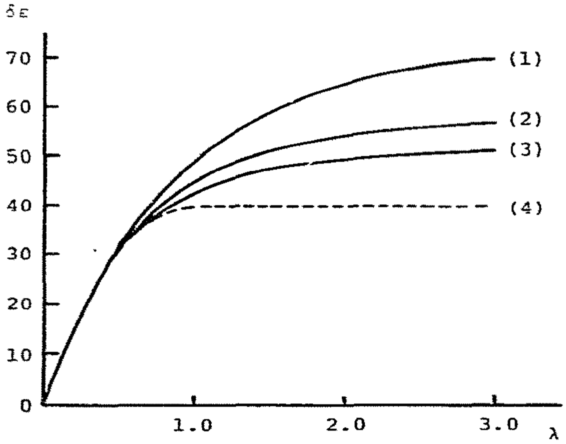

Fig. 2. Dielectric increment due to the distortion of counterions in the absence of counterion-flow. (1) R/a = 9.02; (2) R/a = 28.53; (3) R/a = 90.22 and (4) $R/a \to \infty$.

4.2. The system with counterion flow under the condition of $u_R = 0$

Substituting the solution of $J(r)$, which is a linear combination of J_1 and J_2 into eq. (3.5), we can obtain the final expression of $\delta\epsilon$. The arbitrary constants for J_1 and J_2 are determined by the set of boundary conditions $u_R = 0$ and $J_a = 0$, or $u_R = 0$ and $J_a^{(1)} = 0$. Although the final $\delta\epsilon$ expression is given analytically, it is so complicated that here we will write down the expression for the special case a/R tends zero, which can be described by only J_1 term since J_2 diverges on a tending to zero.

$$\begin{aligned}\delta\epsilon/D = {} & \tfrac{1}{2}\lambda(2 - \lambda) - (2 + \lambda - \tfrac{1}{2}\lambda^2)\{(\lambda^2 + 1)^{1/2} + 1 - \lambda\} \\ & + 2(1 + \lambda^2)^{1/2}(2 + \lambda - \tfrac{1}{2}\lambda^2)\frac{F(\alpha_0, \beta_0, \gamma_0 - 1; S_R)}{F(\alpha_0, \beta_0, \gamma_0; S_R)} \\ & - \frac{2\lambda(2 - \lambda)}{2(1 - \lambda)}[2(1 + \lambda^2)^{1/2} G(\alpha_0, \beta_0, \gamma_0 - 1, l_0; S_R) \\ & - \{(1 + \lambda^2)^{1/2} - \lambda\} G(\alpha_0, \beta_0, \gamma_0, l_0; S_R)] \\ & \times [F(\alpha_0, \beta_0, \gamma_0; S_R)]^{-1}\,,\end{aligned} \tag{4.5}$$

where $\alpha_0, \beta_0, \gamma_0$ and l_0 denote the corresponding quantities α, β, γ and l when $A = 1 - \lambda$ in eq. (3.12), and S_R in this case is given

$$S_R = \lambda/(2 - \lambda)\,.$$

Here the function G is defined by

$$G(\alpha, \beta, \gamma, l; S_R) = \sum_{n=0}^{\infty} \frac{(\alpha)_n (\beta)_n}{n!(\gamma)_n (n + l + 1)} S_R^n\,, \tag{4.6}$$

where $(\alpha)_n = \alpha(\alpha - 1)(\alpha - 2)\ \ldots$, likewise $(\beta)_n$ and $(\gamma)_n$ are defined.

The numerical calculations were performed for various values of a/R and λ. The results are shown in fig. 3, in which the solid lines represent the case of $J_a = 0$ and the dotted lines are for the case $J_a^{(1)} = 0$. In the case of small a/R, the solid and the dotted lines coincide with each other.

It should be noted that $\delta\epsilon$ under the condition of ion-flow in fig. 3 is much smaller than the case without the ion-flow in fig. 2.

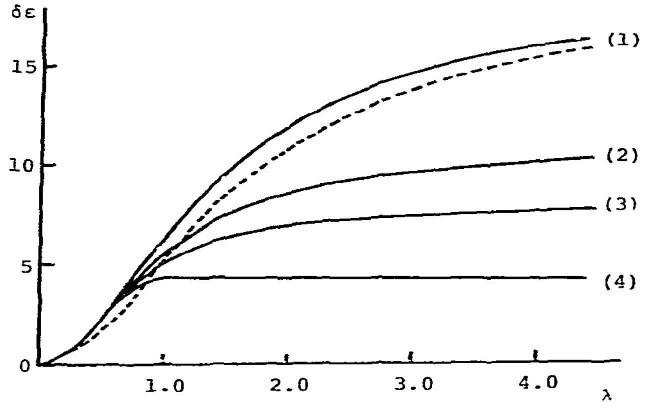

Fig. 3. Dielectric increment due to the distortion of counterions in the presence of counterion-flow. The numbers are the same as in fig. 2. The dotted line is for $J_a^{(1)} = 0$.

5. Discussion

In the treatment of the above calculations, the boundary condition $u_R = 0$ is employed for the case of the existence of counterion-flow. This condition is the case giving the lowest dielectric increment; this fact is examined by the following general $\delta\epsilon$-expression obtained for a finite u_R under the boundary condition $J_a = 0$;

$$\delta\epsilon = (1 + u_R/q_R)\delta\epsilon_0 - (u_R/q_R)\delta\epsilon_1 \, , \tag{5.1}$$

where $\delta\epsilon_0$ is $\delta\epsilon$ for the case of $u_R = 0$, and $\delta\epsilon_1$ is $\delta\epsilon$ for the case of $J = 0$, that is $q_R = -u_R$, shown in eq. (4.1). This relation, the proof of which is shown in Appendix, gives the dielectric increment for arbitrary values of u_R, connecting the $\delta\epsilon$ for the case of $u_R = 0$ with that for the case of $J = 0$.

The concept of the free-volume assumed here under the electric field is based on the model of the cave for a single polyion and its counterions hollowed in the macroscopic polyion solution. It is still an unsolved problem how to determine the most reasonable condition for u_R in this cave model. On the other hand, the condition of non ion-flow, $J = 0$, is thought to be an ideal but physically likely and important condition in this system, since this condition is not accompanied by Joule energy-dispertion in the free-volume.

Since each polyion has a thermal free rotation together with its free-volume, it should be noted that the values of $\delta\epsilon$ obtained above must be multiplied by 2/3.

As shown in fig. 3, the $\delta\epsilon$-values under condition $J_a = 0$ are not so different from those under the condition $J_a^{(1)} = 0$. This implies that the setting of the boundary condition on the polyion surface is not so important especially in the case a/R is small.

As described in sect. 2, the fundamental equation (2.17) is thought to be available when $\omega R^2/D_f \ll 1$. The frequency range satisfying this condition is roughly calculated to be less than 100 kHz, for example if D_f of the counterion is 10^{-5} cm^2/s as usual and R is taken to be 2×10^{-6} cm (which corresponds to 5 mN solution of sodium-polyacrylic acid), the value of $\omega R^2/D_f$ becomes to be an order of magnitude 10 MHz. The dielectric increment observed in the experiments at the higher frequency side (100 kHz-order) had the same order value as our results in fig. 2 [11]. Accordingly, the origin of the dielectric constant in 100 kHz-range may be attributed to the present mechanism that is the distortion of the spatial counterion distribution around polyion.

A similar calculation has been done by us for the case of rigid spherical colloidal systems, which can be done only by a computer analysis of the equations. This gives also fairly noticeable $\delta\epsilon$ values. This result will be also published elsewhere.

Appendix

Eq. (5.1) can be derived in the following way. If we adopt the boundary conditions $q_a = 0$ and $J_a = 0$ as employed above, $J(r)$ in the case of finite u_R must be expressed as

$$J(r) = (u_R + q_R)\, j(r) \, , \tag{A.1}$$

with a function $j(r)$ having no arbitrary constants to be determined from the boundary conditions. If we define $J^0(r)$ for $J(r)$ when the boundary $u_R = 0$ is set, this $J^0(r)$ should be written with the same $j(r)$ as (A.1) in the form;

$$J^0(r) = q_R\, j(r) \, . \tag{A.2}$$

On the other hand, if $u(r)$ and $q(r)$ for the case $u_R = 0$ are denoted by $u^0(r)$ and $q^0(r)$, respectively, these $u^0(r)$ and $q^0(r)$ should be expressed by

$$u^0(r) = q_R U(r) \, , \quad q^0(r) = q_R Q(r) \, , \tag{A.3}$$

with functions $U(r)$, $Q(r)$ having no integral constants determined by the boundary conditions. Of course, $U(r)$ and $Q(r)$ must satisfy the basic equation (2.14);

$$\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r} rQ = -\kappa^2 e^{-\phi_0} U\,. \qquad \text{(A.4)}$$

Since $J^0(r) = u^0(r) + q^0(r)$, the eqs. (A.2) and (A.3) lead to the relation

$$j(r) = U(r) + Q(r)\,,$$

and hence, from eq. (A.1) we have

$$J(r) = u(r) + q(r) = (u_R + q_R)\{U(r) + Q(r)\}\,,$$

that is

$$q(r) = (u_R + q_R)\{U(r) + Q(r)\} - u(r)\,. \qquad \text{(A.5)}$$

By substituting eq. (A.5) into eq. (2.14) and refering to eq. (A.4), we have a differential equation for a function $[(u_R + q_R)U(r) - u(r)]$, such that

$$\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r} r\{(u_R + q_R)U(r) - u(r)\}$$

$$= \kappa^2 e^{-\phi_0}\{(u_R + q_R)U(r) - u(r)\}\,. \qquad \text{(A.6)}$$

This equation can be solved, under the condition of eq. (2.6) for ϕ_0 and the present boundary conditions $u_a = 0$ and $u(R) = u_R$, in the form:

$$u(r) = (1 + u_R/q_R)u^0(r)$$

$$- u_R \kappa^2 R \phi_0^{(1)} \int_a^r \mathrm{d}r/r(\phi_0^{(1)})^2\,, \qquad \text{(A.7)}$$

in which $U(r)$ in eq. (A.6) is replaced by $u^0(r)$ given in eq. (A.3). Substituting eq. (A.7) into eq. (2.18) we can obtain the relation between the dipolemoment due to $u(r)$ when u_R is finite and that due to $u^0(r)$ when $u_R = 0$. From this relation we obtain eq. (5.1) after substituting the concrete form $\phi_0^{(1)}$ in eq. (3.6).

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