Theory of Electrolytic Solution Computing Ion-Dipole Interaction
I. Dielectric Properties

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The dielectric properties of electrolytic solutions have been treated theoretically based on the consideration of ion-dipole interaction. The magnitude of ion-dipole interaction have been calculated by assuming a suitable model for solution. Theoretical formulae for relaxation time, dielectric constant, and loss factor of electrolytic solution have been obtained. The formula in the limiting case of a dilute solution, is identical with that of Sack and Debye.

I. Introduction

The dielectric properties of electrolytic solution are different from those of pure solvent, though we neglect ion conductivity. The reason of this difference is based on (i) the interaction between ions and (ii) ion-dipole interaction. The magnitude of former effect was calculated quantitatively by Debye and Falkenhagen.(1) The latter effect was early pointed out by Mizushima,(2) but quantitative calculation of this effect was difficult. The approximate methods of calculating this effect can be made in two different ways. (a) We consider a dipole located at the center of the dipole field, which affects the motions of ions. This method was developed by Oka.(3) (b) We consider an ion as a center of ionic field which affects the motions of dipoles. Sack(4) and Debye(5) succeeded in calculating dielectric constant of dilute electrolytic solution from the latter point of view, but they could not calculate relaxation time and dielectric loss factor.

In the present paper we shall calculate dielectric constant, loss factor and relaxation time of strong electrolytic solution according to the method (b) which is, however, different from that of Sack and Debye.

When an electrolyte is dissolved into a polar solvent, the dipoles of the solvent will be arranged around an ion by the ionic field. If an external electric field is applied to this solution, motions of solvent dipoles will be different from those of pure solvent, owing to the presence of the ionic field, which hinders the rotation of dipoles. Thus the motions of dipoles will become elastic, and the mean moment of a dipole will be reduced. At the same time, the mean relaxation time will be smaller.

Based on the following model, we shall treat this phenomena quantitatively.

II. Model and Hypotheses Used

(1) For the sake of convenience in calcuation we assume the following model for a structure of solution. We consider a conducting shell of radius β_j with electric charge $-z_je$ around an ion of radius α_j with electric charge z_je, where z_j denotes valency of j-th ion, and $-e$, the electronic charge. Between an ion and a shell lie dipoles, and a solution is filled up by these shells.

If we assume this model for the solution, a dipole of solvent at the distance r from the center of an ion, has potential energy $-\mu z_je/r^2$ from α_j to β_j, and when $r>\beta_j$, its value becomes zero suddenly. Here μ denotes effective moment, which depends on r, but as a first approximation we shall assume that it has a constant value.

(2) We shall further assume that the relaxation time of ionic atmosphere (Ionenwolke) has a different order of magnitude from that of dipole rotation; so that we may consider them separately.

(3) The resistance of media against dipole rotation will be assumed to obey Stokes' law of hydrodymamics, and the viscosity coefficient, which appears in Stokes' expression, has the same magnitude as that of macroscopic viscosity.

(4) The distribution function of dipoles f is assumed to be independent of r (distance from the center of an ion).

III. Fundamental Equation and its Solution

To know the change of relaxation time, dielectric constant and loss factor caused by the introduction of electrolyte into the solvent, we have to calculate the mean relaxation time, and the mean electric moment under the influence of ionic field when the external field is applied.

If f denotes the distribution function of

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(1) Debye and Falkenhagen, *Physik. Z.*, **29**, 128, 402 (1928).

(2) S. Mizushima, *Jour. Chem. Soc. Japan*, **49**, 1 (1928).

(3) Syoten Oka, *Proc. Phy-Math. Soc. Japan*, **17**, 454 (1935).

(4) H. Sack, *Physik. Z.*, **28**, 199 (1927).

(5) P. Debye, "Polare Molekeln", Leipzig (1929).

dipoles in a shell in an external field, f satisfies the following equation.(6)

$$\frac{\partial f}{\partial t}=\frac{kT}{\rho}\Delta f+\frac{1}{\rho}\operatorname{div}(f\operatorname{grad}u) \qquad (1)$$

where u denotes potentioal energy of a dipole;

$$u=u_0+u_1 e^{i\omega t} \qquad (2)$$

$$u_0=-\frac{\mu e z_j}{r^2}\cos\vartheta \qquad (3)$$

$$u_1=-\mu F\cos\vartheta'. \qquad (4)$$

In these equations u_0 is the potential energy of a dipole in the absence of the external field. ϑ is the angle between the axis of dipole and a line which joins the center of dipole with that of ion. u_1 is the potential energy due to an external field. ϑ' is the angle between the electric field vector and dipole axis. ρ denotes the resistance constant and is expressed as

$$\rho=8\pi\eta a^3 \qquad (5)$$

according to the assumption (3) of II. η is the viscosity coefficient, a, the radius of a sphere of dipole, ω, circular frequency, k the Boltzmann constant, T, the absolute temperature and t, the time.

By assumption (4) of II, Eq. (1) is to be solved on the condition of r=constant. The mean electric moment $\overline{\mu}_{jr}$ on the surface of shell r=constant around j-th ion is evaluated according to the method developed by Kubo.(7)

The result obtained is as follows:

$$\overline{\mu}_{jr}=\frac{F e^{i\omega t}}{kT}\cdot\frac{\mu^2 R}{3}\,\frac{1}{1+i\omega\bar{\tau}_{jr}} \qquad (6)$$

where R represents the reduction factor

$$R=1-L^2(y) \qquad (7)$$

$$y=\frac{\mu e z_j}{r^2 kT} \qquad (8)$$

and L is the Langevin function. $\bar{\tau}_{jr}$ is the mean relaxation time on a shell r=constant and has the following form:(8)

$$\bar{\tau}_{jr}=\frac{2}{2kT}R. \qquad (9)$$

The mean relaxation time and mean electric moment of dipoles located in the said spheric shell are represented as follows:

$$\bar{\tau}_j=\frac{\rho}{2kT}\int_{\alpha_j}^{\beta_j}\{1-L^2(y)\}\cdot 4\pi r^2\,\mathrm{d}r\Big/\int_{\alpha_j}^{\beta_j}4\pi r^2\,\mathrm{d}r \qquad (10)$$

$$\overline{\mu}_j=\gamma_j F e^{i\omega t} \qquad (11)$$

where

$$\gamma_j=\frac{\mu^2}{3kT}\int_{\alpha_j}^{\beta_j}\frac{\{1-L^2(y)\}}{1+i\omega\bar{\tau}_{jr}}\cdot 4\pi r^2 dr\Big/\int_{\alpha_j}^{\beta_j}4\pi r^2\,\mathrm{d}r. \qquad (12)$$

The mean relaxation time and the mean electric moment (of whole solution) have the following forms:

$$\begin{aligned}\bar{\tau}&=\sum n_j(\beta_j^3-\alpha_j^3)\bar{\tau}_j/\sum n_j(\beta_j^3-\alpha_j^3)\\ \overline{\mu}&=Fe^{i\omega t}\cdot\sum n_j(\beta_j^3-\alpha_j^3)\gamma_j/\sum n_j(\beta_j^3-\alpha_j^3)\\ &=Fe^{i\omega t}\cdot\gamma. \end{aligned} \qquad (14)$$

IV. Relaxation Time, Dielectric Constant and Loss Factor of Electorolytic Solution

A. Relaxation Time.—It can be seen from Eq. (9) that an electrolytic solution must have many relaxation times instead of one. However, to obtain a rough estimation, we can replace them by their mean value (Eq. (13)). Especially when we deal with dilute solution, the use of mean value will be a good appoximation. This mean value is represented by Eq. (13). (see also Eq. (10)).

B. Dielectric Constant and Loss Factor.—Dielectric constant (complex) ε consists of two parts, the first part coming from solvent molecules and the second part from ions. We assume simply that ε is obtained by the addition of these two parts, i. e.

$$\varepsilon=\varepsilon_d+\varepsilon_i \qquad (15)$$

where ε_d is the part of solvent molecules and ε_i, of ions. ε_i can be calculated by the Debye-Falkenhagen theory.(1)(9) (We do not write its formula explicitly.)

It seems to us that there is no satisfactory relation between ε_d and the mean electric moment $\overline{\mu}$ or γ, but we assume tentatively Clausius-Mosotti's hypothesis, i. e.,

$$\left\{\frac{\varepsilon_d-1}{\varepsilon_d+2}-\frac{n^2-1}{n^2+2}\right\}V_0-P_A=\frac{4\pi}{3}\gamma, \qquad (16)$$

where γ is represented by Eq. (14). V_0 denotes molecular volume, P_A, atomic polarization, and n, refractive index of solution.

ε_d has real and imaginary parts,

$$\varepsilon_d=\varepsilon_d'-i\varepsilon_d''. \qquad (17)$$

Calculating γ from Eq. (14), we can obtain ε_d by the use of Eq. (16). The real part of

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(6) Debye and Ramm, *Ann. Physik*, **28**, 28 (1937).

(7) Ryôgo Kubo, *Nippon Sûgaku-Buturigaku-kaisi*, **16**, 293 (1942).

(8) The dipoles on spherical shell r=constant have many relaxation times, i. e., τ_{jr}'s instead of one, because the dipoles are affected by the ionic field.(6)(7) However, these relaxation times are not so widely distributed(7) that we can use their mean value $\bar{\tau}_{jr}$ without serious errors.

(9) H. Falkenhagen, "Electrolytes" Oxford University Press, London (1934).

ε_d (ε_d') denotes the dielectric constant and the imaginary part (ε_d''), the loss factor due to solvent molecules. If we know ε_d, we can calculate total dielectric constant (complex) ε from Eq. (15).

V. β_j

To evaluate ε_d, we must know γ_j. To calculate γ_j we must know β_j. β_j may be called ***effective Screening radius***, and is generally dependent on temperature, solvents, solute, and the concentration of solution. We shall consider most possible forms of β_j.

A. Static Model.—As $\frac{4\pi}{3}\beta_j^3$ is the volume of afore-described sphere, $\sum\frac{4\pi}{3}\beta_j^3 n_j$ will be proportional to the volume apportioned to $\sum n_j$ ions, i.e., to the unit volume, when we adopt static model.

$$\frac{4\pi}{3}\sum n_j\beta_j^3 = K^3 \tag{18}$$

Here K represents a constant, which is independent of above-mentioned variables. Using this model we can derive the Sack-Debye formula(4)(5) for dielectric constant of dilute solution. We shall discuss later this problem.

B. Dynamical or Statistical Model.—Considering thermal motions of ions, β_j should be dependent on temperature, electrolyte, solvent, and the concentration of solution. We assume that β_j is proportional to radius of ionic cloud $1/\kappa$, which appears in Debye-Hückel theory,(9)(10) i.e.,

$$\beta_j = \frac{A}{\kappa} = A\left(\frac{\varepsilon_0' kT}{4\pi e^2\sum n_j z_j^2}\right)^{\frac{1}{2}} \tag{19}$$

where ε_0' is static dielectric constant of the solvent.

VI. Evaluation of Relaxation Time, Dielectric Constant and Loss Factor

A. Relaxation Time.—The mean relaxation time is represented by Eq. (13). The mean relaxation time of dipoles around j-th ion is represented by Eq. (10). The following is the formula rewritten:

$$\bar{\tau}_j = \tau_0\int_{\alpha_j}^{\beta_j}\{1 - L^2(y)\}\cdot 4\pi r^2\,\mathrm{d}\,r \Big/ \int_{\alpha_j}^{\beta_j} 4\pi r^2\mathrm{d}\,r \tag{10}$$

$$\tau_0 = \rho/2kT \tag{10'}$$

To obtain the value of $\bar{\tau}_j$, it is necessary to calculate

$$\int_{\alpha_j}^{\beta_j}\{1 - L^2(y)\}\cdot 4\pi r\,\mathrm{d}\,r. \tag{20}$$

The integration is difficult, but this value can be evaluated as follows. Divide the integration into three parts as follows:

$$\int_{\alpha_j}^{\beta_j} = \int_{\alpha_j}^{\frac{b_j}{2}} + \int_{\frac{b_j}{2}}^{\frac{3}{2}b_j} + \int_{\frac{3}{2}b_j}^{\beta_j}, \tag{21}$$

where b_j is defined by Eq. (22).

$$b_j = z_j^{1/2}\left(\frac{\mu e}{kT}\right)^{1/2} \tag{22}$$

b_j is the value of r which makes $y = 1$, i.e., the distance at which the potential energy $\mu e z_j/r^2$ is equal to kT.

In the first term of the right hand side of Eq. (21), $L(y)$ can be replaced by $1-1/y$, for $(y)_{r=bj/2} = 4$, $L(4) \doteqdot 1-1/4$. In the third term, we can replace $L(y)$ by $y/3$, for $(y)_{r=3b_j/2} = 4/9$, $L(4/9) = 0.1469 \doteqdot 1/3(4/9) = 0.1480$.

The second part can be transformed into the following form, according to the first mean value theorem of integration calculus.(11)

$$\int_{\frac{1}{2}b_j}^{\frac{3}{2}b_j}\{1 - L(y)\}4\pi r^2\,\mathrm{d}\,r$$

$$= \{1-L^2(\xi)\}\int_{\frac{1}{2}b_j}^{\frac{3}{2}b_j} 4\pi r^2\,\mathrm{d}\,r$$

$$= 4\pi\{1 - L^2(\xi)\}\cdot\frac{13}{12}b_j^3$$

$$(4 > \xi > 4/9)$$

The integral (21) can be rewritten as follows:

$$\begin{aligned}
\int_{\alpha_j}^{\beta_j}\{1 - L^2(y)\}4\pi r^2\,\mathrm{d}\,r &= 4\pi\Bigg[\int_{\alpha_j}^{\frac{b_j}{3}}\frac{2r^4}{b_j^2}\,\mathrm{d}\,r \\
&\quad + \frac{13}{12}\{1 - L^2(\xi)\}b_j^3 + \int_{\frac{3}{2}b_j}^{\beta_j}\left(1 - \frac{b_j^4}{9r^4}\right)r^2\,\mathrm{d}\,r\Bigg] \\
&= 4\pi\left[\frac{1}{3}\beta_j^3 - \left\{0.103 + \frac{13}{12}L^2(\xi)\right\}b_j^3 \right. \\
&\quad \left. - \frac{2}{5}\frac{\alpha_j^5}{b_j^2} + \frac{1}{9}\frac{b_j^4}{\beta_j}\right] \\
&\doteqdot \frac{4\pi}{3}\left[\beta_j^3 - 3\left\{0.103 + \frac{13}{12}L^2(\xi)\right\}b_j^3 \right. \\
&\quad \left. + \frac{1}{3}\frac{b_j^4}{\beta_j}\right]
\end{aligned} \tag{23}$$

This formula holds only when $\beta_j > 3/2\,b_j$ (i.e., solution not concentrated).

Here we neglected $2/5\ (\alpha_j^5/b_j^2)$, considering it very small. Considering α_j^3 small as compared with β_j^3, we can approximately rewrite Eq. (10) as follows,

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(10) Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

(11) See, Whitaker and Watson, "Modern Analysis," p. 65, 4 th edition (1935).

$$\bar{\tau}_j \doteqdot \tau_0 \left[1 - 3\left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \left(\frac{b_1}{\beta_j} \right)^3 + \frac{1}{3} \left(\frac{b_j}{\beta_j} \right)^4 \right] \tag{24}$$

Using Eqs. (22) and (18) or (19), $\bar{\tau}_j$ can be calculated, and $\bar{\tau}$ also. (by Eq. (13)).

B. Static Dielectric Constant ($\omega = 0$).—The static field is specified by the notation ∞ ($\lambda = \infty$).

$$\gamma_{j\infty} = \frac{\mu^2}{3kT} \int_{\alpha_j}^{\beta_j} \{1 - L^2(y)\} 4\pi r^2 \,\mathrm{d}r \Big/ \int_{\alpha_j}^{\beta_j} 4\pi r^2 \,\mathrm{d}r \tag{25}$$

This formula can be evaluated according to the same procedure as relaxation time.

$$\gamma_{j\infty} \doteqdot \frac{\mu^2}{3kT} \left[1 - 3\left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \left(\frac{b_j}{\beta_j} \right)^3 + \frac{1}{3} \left(\frac{b_j}{\beta_j} \right)^4 \right] \tag{26}$$

Static dielectric constant $\varepsilon_{d\infty}$ can be calculated from the following equation:

$$\left\{ \frac{\varepsilon_{d\infty} - 1}{\varepsilon_{d\infty} + 2} - \frac{n^2 - 1}{n^2 + 2} \right\} V_0 - P_A = \frac{4\pi}{3} \gamma_\infty, \tag{27}$$

where

$$\gamma_\infty \doteqdot \frac{\sum n_j \gamma_{j\infty} \beta_j^3}{\sum n_j \beta_j^3}. \tag{28}$$

For dilute solutions, we can derive limiting formula. By differentiation of Eq. (27) we can obtain

$$\begin{aligned} \Delta\varepsilon_d &= \frac{4\pi}{3} \frac{(\varepsilon_0' + 2)^2}{3V_0} \Delta\gamma_\infty \\ &\doteqdot -\frac{4\pi}{3} \frac{(\varepsilon_0' + 2)^2}{3V_0} \frac{\mu^2}{3kT} \left[3\left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \right] \left(\frac{\sum n_j b_j^3}{\sum n_j \beta_j^3} \right) \end{aligned} \tag{29}$$

where

$$n_j = \frac{Nc}{10^3} \nu_j \tag{30}$$

and N is Avogadro's number, c, concentration in mole per liter, and ν_j, number of j-th ions in electrolyte molecule.

Using static model, β_j is represented by Eq. (18). Eq. (29) is rewritten as follows.

$$\begin{aligned} \Delta\varepsilon_d = &-\left(\frac{4\pi}{3} \cdot \frac{\mu^2}{3kT} \right) \left(\frac{(\varepsilon_0' + 2)^2}{3V_0} \right) \left(\frac{4\pi}{3} \right) \\ &\left[3\left\{ 0.103 + \frac{13}{12} L^2(\xi) \right\} \right] \left(\frac{\mu e}{kT} \right)^{\frac{3}{2}} \cdot \\ &\left(\frac{Nc}{10^3 K^3} \right) \sum \nu_j z_j^{\frac{3}{2}} = -B \times c \sum \nu_j z_j^{\frac{3}{2}} \end{aligned} \tag{31}$$

B represents a constant independent of c, ν_j and z_j.

Sack and Debye derived an equation for the dielectric constant of dilute electrolytic solution.(4)(5)

$$\varepsilon_{d\infty} = \varepsilon_0' (1 - B' c \sum \nu_j z_j^{\frac{3}{2}}). \tag{32}$$

Eq. (31) has a similar form as Eq. (32). They detemined B' experimentally and obtained a value 3.3 at room temperature.(12) If we put $K^3 = 2$ (all the spheres of radii β_j's belonging to the ions of the same sign just fill up the whole solution), Eq. (31) can be rewritten at 20° as follows, ($\varepsilon_0' = 80.1$, $V_0 = 18.05$, $\mu = 0.8168\mathrm{D}$).(13)

$$\Delta\varepsilon_{d\infty} = 2.64 \times 10^2 c \sum \nu_j z_j^{\frac{3}{2}}$$

or

$$\varepsilon_{d\infty} = 80.1\{1 - 3.3\, c \sum \nu_j z_j^{\frac{3}{2}}\}. \tag{33}$$

The constant B' is found to be 3.3.(14) This value agrees well with that of Sack and Debye 3.3 obtained experimentally, but this numerical agreement is rather fortuitous, since we have used so many hypotheses and simplifications.

Assuming dynamical model $\Delta\varepsilon_{d\infty}$ is written as follows from Eqs. (29), (19) and (22).

$$\begin{aligned} \Delta\varepsilon_{d\infty} = &-\frac{4\pi}{3} \cdot \frac{\mu^2}{3kT} \cdot \frac{(\varepsilon_0' + 2)^2}{3V_0} \cdot \\ &\frac{[3\{1.03 + \frac{13}{12} L^2(\xi)\}]}{A^3} \cdot \left(\frac{\mu e}{kT} \right)^{\frac{3}{2}} \cdot \\ &\left(\frac{4\pi e^2}{\varepsilon_0' kT} \right)^{\frac{3}{2}} N^{\frac{3}{2}} c^{\frac{3}{2}} \frac{\sum \nu_j z_j^{\frac{3}{2}}}{\sum \nu_j} (\sum \nu_j z_j^2)^{\frac{3}{2}} \\ = &-B'' c^{\frac{3}{2}} \frac{(\sum \nu_j z_j^{\frac{3}{2}})}{\sum \nu_j} \times (\sum \nu_j z_j^2)^{\frac{3}{2}} \end{aligned} \tag{34}$$

$\Delta\varepsilon_{d\infty}$ is proportional to $c^{\frac{3}{2}}$.

For dilute solutions, experimental values of $\Delta\varepsilon_{d\infty}$ are so inconsistent that we cannot see whether Eq. (31) or (34) is valid. We hope that reliable experimental values will appear in the near future.

C. Dielectric Constant and Loss Factor in Non-Static Case.—Dielectric constant and loss factor in non-static field ($\omega > 0$) are calculated from Eqs. (12), (14) and (16), but this calculation is very laborious though not impossible. For a rough estimation, there is a simpler mothod. We assume that an electrolytic solution has a single relaxation time which is represented by $\bar{\tau}$ (Eq. (13)). Then the complex dielectric constant is calculated by the following equation.

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(12) There are many experimental values that are not represented by Eq. (32), cf. ref. (5).

(13) This value is obtained from the equation $\left(\frac{\varepsilon_0' - 1}{\varepsilon_0' + 2} - \frac{n^2 - 1}{n^2 + 2} \right) V_0 = \frac{4\pi}{3} \frac{\mu^2}{3kT}$. It is much smaller than that of gas.

(14) In order to obtain the value of B, we assume that $L^2(\xi) = {}^1/_2\{L^2(4) + L^2(4/9)\} = 0.294$ in Eq. (31), so that the numerical value in Eq. (33) is rather ambiguous.

$$\left(\frac{\varepsilon_d-1}{\varepsilon_d+2}-\frac{n^2-1}{n^2+2}\right)V_0-P_A=\frac{4\pi}{3}\gamma_\infty\frac{1}{1+i\omega\bar{\tau}}\ . \tag{35}$$

γ_∞ and $\bar{\tau}$ are evaluated by Eqs. (26), (28), (13) and (24). A convenient method to calculate ε_d' and ε_d'' from $\bar{\tau}$ and γ_∞ is given by Debye.(5)

D. Dielectric Properties at Long Wave Length Region ($\omega\bar{\tau}\ll1$).—In this case γ_j is represented approximately as follows. Divide γ_j into two parts, i.e.,

$$\gamma_j=\gamma_j'-i\gamma_j'' \tag{36}$$

$$\begin{aligned}\gamma_j'&=\frac{\mu^2}{3kT}\int_{\alpha_j}^{\beta_j}\frac{\{1-L^2(y)\}}{1+\omega^2\bar{\tau}_j^{\,2}}\cdot4\pi r^2\,\mathrm{d}\,r\Bigg/\int_{\alpha_j}^{\beta_j}4\pi r^2\,\mathrm{d}\,r\\&\doteqdot\frac{\mu^2}{3kT}\int_{\alpha_j}^{\beta_j}\{1-L^2(y)\}4\pi r^2\,\mathrm{d}\,r\Bigg/\int_{\alpha_j}^{\beta_j}4\pi r^2\,\mathrm{d}\,r.\end{aligned} \tag{37}$$

This integration is evaluated already and is equal to $\gamma_{j\infty}$ (Eq. (26)).

$$\gamma_j''=\frac{\mu^2\omega\tau_0}{3kT}\int_{\alpha_j}^{\beta_j}\{1-L^2(y)\}^2 4\pi r^2\mathrm{d}r\Bigg/\int_{\alpha_j}^{\beta_j}4\pi r^2\mathrm{d}r. \tag{38}$$

Eq. (38) can be evaluated by a similar procedure as in the case of $\gamma_{j\infty}$, but writing out its formula here will be omitted.

E. Dielectric Properties at Short Wave Length Region ($\omega\bar{\tau}\gg1$).—In this case $\gamma_j'\doteqdot0$ and $\gamma_j''\doteqdot(\mu^2/3kT)\times(1/\omega\tau_0)$. It means that in this region the properties of electrolytic solution are almost the same as those of pure solvent.

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