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Transient electric birefringence of colloidal particles immersed in shear flow. Part II. The initial response under the action of a rectangular electric pulse and the behavior at a low alternating electric field

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Abstract

The time-dependent rotational diffusion equation for rigid macromolecules in solution has been approximately solved for two cases in order to extend the electric birefringence technique to streaming-electric birefringence. One is for the initial period through the application of a rectangular electric pulse to the solution immersed in a low shear flow. The purpose of this is expansion of the distribution function into a function series made by the product of the powers of reduced time ($=\Theta t$) and hydrodynamic field α ($=G/\Theta$, G: velocity gradient, Θ: rotary diffusion constant) and a surface harmonic P_i^j cos $j\phi$. The solution for the build-up process at arbitrary electric field strength is found, but is limited to low hydrodynamic fields. The other is for the response when an alternating electric field is applied to the solution in a shear flow. Here, instead of reduced time, the maximum electric field E_0 is chosen as a parameter for the expansion. The expressions for the intensity of the transmitted light through crossed Nicols are derived in two optical systems where the polarizer is set at an angle of 45° and 0° to the direction of the electric field. The results in the former case show that we can determine four parameters, the ratio of velocity gradient to rotary diffusion constant, the axial ratio of a particle, the anisotropy of electric polarizability, and the optical anisotropy factor, from four values observed in two optical systems, namely, two light intensities before applying an electric field and two initial slopes of the build-up after applying an electric field. On the other hand, when a low alternating electric field with extremely high frequency is applied, the build-up of the light intensity in the former case is the same as that of electric birefringence for pure induced dipole orientation. The build-up for the latter optical system is the same as the expression for pure induced dipole orientation of Eq. (38) shown in a previous work.

Keywords: Colloids; Transient electric birefringence

1. Introduction

The measurement of electric birefringence is very sensitive, thus making possible measurement at dilute concentrations and for small-scale samples. Moreover, it gives us various kinds of information such as the electric, optical, and hydrodynamic properties of the solute. However, we can neither directly determine whether the shape of the solute particle with geometrical symmetric axis is prolate or oblate nor determine any of the

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signs of the optical anisotropy factor and the anisotropy of electric polarizability. In order to make up for this deficiency, some authors [1–4] have proposed a method of electric birefringence measurement under a steady-state shear flow. Moreover, Kobayashi has tried to extend the transient electric birefringence under a shear flow [5]. In order to improve this method we have found the approximate expressions of transient electric birefringence and extinction angle up to the fourth power of an electric field and/or velocity gradient in a previous paper [6]. There, the angular distribution function was expanded into a function series made up of the product of the powers of the electric and hydrodynamic fields and a surface harmonic. In this paper, we will try to extend two techniques of electric birefringence to streaming-electric birefringence measurement. One is the method analyzing the initial slope or the initial response of birefringence just after a rectangular electric pulse is applied. For this purpose, the distribution function is expanded into a power series of reduced time instead of the electric field, as was done for electric birefringence in previous papers [7–12]. It will be possible to derive the distribution at arbitrary electric fields even for streaming-electric birefringence, although it is limited to the initial period.

The other is the response under an alternating electric field. The electric birefringence under a sinusoidal electric field such as $E = E_0\cos\,\omega t$ or $E = E_0\sin\,\omega t$, is also discussed by some authors [13–16]. When a high frequent alternating electric field is used, only induced dipole moments are effective to the orientation of macromolecules. Therefore, we can confirm the contribution of the induced dipole moment to the orientation of macromolecules. If we can extend this method to the streaming electric birefringence method, we will be able to obtain information about the axial ratio of macromolecule at the same time as well as the parameters obtained by electric birefringence.

2. Theory

2.1. The initial distribution function under the action of a rectangular electric pulse

As in a previous paper [6], let us start by considering the angular distribution function of an axially symmetric solute particle both with a permanent dipole moment and with an induced dipole moment. These symmetric axes are assumed to coincide with the common axis with respect to optical property and hydrodynamical property of the solute. The distribution function F satisfies the following diffusion equation;

$$\left(\frac{1}{\Theta}\frac{\partial}{\partial t} - \boldsymbol{D}\right)F = \boldsymbol{P}F + \boldsymbol{I}F + \alpha\boldsymbol{S}F, \qquad (1)$$

where operators $\boldsymbol{D}$, $\boldsymbol{P}$, $\boldsymbol{I}$ and $\boldsymbol{S}$ are

$$\boldsymbol{D} = \frac{\partial}{\partial u}\left[(1-u^2)\frac{\partial}{\partial u}\right] + \frac{1}{1-u^2}\frac{\partial^2}{\partial\phi^2}$$

$$\boldsymbol{P} = \beta\left[2u - (1-u^2)\frac{\partial}{\partial u}\right],$$

$$\boldsymbol{I} = 2\gamma\left[(3u^2-1) - u(1-u^2)\frac{\partial}{\partial u}\right],$$

and

$$\boldsymbol{S} = \frac{1+R}{2}\left[(1-u^2)^{1/2}\cos\phi\frac{\partial}{\partial u} + \frac{u}{(1-u^2)^{1/2}}\sin\phi\frac{\partial}{\partial\phi}\right] + R(1-u^2)^{1/2}\cos\phi\left[3u - (1-u^2)\frac{\partial}{\partial u}\right].$$

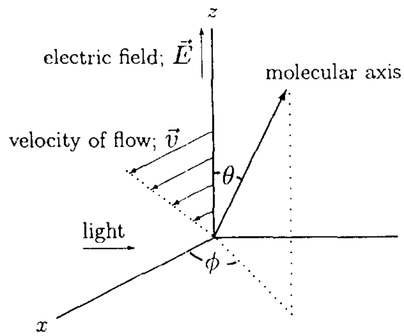

Fig. 1. Coordinate system of an axially symmetric particle in laminar flow, $\vec{v}=(Gz,0,0)$, and electric field, $\vec{E}=(0,0,E)$.

Here, $u=\cos\theta$, $\alpha=G/\Theta$, $\beta=\mu' E/kT$, $\gamma=(\alpha_1-\alpha_2)E^2/2kT$, and $R=(p^2-1)/(p^2+1)$. θ is the angle between the molecular axis and the electric field $\vec{E}=(0,0,E)$, as shown in Fig. 1. ϕ is the angle between the x axis and the projection of the molecular axis on the horizontal plane.

The velocity of flow $\vec{v}=(Gz,0,0)$ only has as a component of the direction perpendicular to both the incident light and the electric field; G is the velocity gradient. Parameters, μ', $(\alpha_1-\alpha_2)$, Θ, and p are respectively the apparent permanent dipole moment, the anisotropy of electric polarizability, the rotational diffusion coefficient, and the axial ratio of a rotational symmetric solute particle. Other notations are used with their usual meanings. Let's expand the angular distribution function into the function series made by the product between the powers of α and reduced time $(t\Theta)$ and a surface harmonic as follows:

$$F=\Sigma\Sigma\Sigma\Sigma\, K_{ij}^{kl}\alpha^k(\Theta t)^l P_i^j\cos j\phi, \tag{2}$$

where P_i^j is the associated Legendre function of order i and degree j. After inserting Eq. (2) into Eq. (1), let's set each coefficient of the powers of α and Θt as equal to zero. Additionally, using the property of the orthogonal function, we can obtain recurrence relations of K_{ij}^{kl},

$$\begin{aligned}(l+1)K_{ij}^{k,l+1}+i(i+1)K_{ij}^{kl}\\ =d_{i,j-1}K_{i,j-1}^{k-1,l}+d_{i,j+1}K_{i,j+1}^{k-1,l}+d_{i-2,j-1}K_{i-2,j-1}^{k-1,l}+d_{i-2,j+1}K_{i-2,j+1}^{k-1,l}+d_{i+2,j-1}K_{i+2,j-1}^{k-1,l}\\ +d_{i+2,j+1}K_{i+2,j+1}^{k-1,l}+d_{i-1,j}K_{i-1,j}^{k,l}+d_{i+1,j}K_{i+1,j}^{k,l}+d_{i-2,j}K_{i-2,j}^{k,l}+d_{i,j}K_{i,j}^{k,l}+d_{i+2,j}K_{i+2,j}^{k,l},\end{aligned} \tag{3}$$

where

$$d_{i,j-1}=\frac{1+R}{4}-\frac{R}{2}\left[\frac{(i-2)(i+j-1)}{(2i-1)(2i+1)}+\frac{(i+3)(i-j+2)}{(2i+1)(2i+3)}\right],$$

$$d_{i,j+1}=-(i-j)(i+j+1)\left\{\frac{1+R}{4}-\frac{R}{2}\left[\frac{(i-2)(i-j-1)}{(2i-1)(2i+1)}+\frac{(i+3)(i+j+2)}{(2i+1)(2i+3)}\right]\right\},$$

$$d_{i-2,j-1}=\frac{R}{2}\frac{(i+1)(i-j)}{(2i-1)(2i-3)},\ d_{i-2,j+1}=-\frac{R}{2}\frac{(i+1)(i-j)(i-j-1)(i-j-2)}{(2i-1)(2i-3)},$$

$$d_{i+2,j-1} = \frac{R}{2}\frac{i(i+j+1)}{(2i+3)(2i+5)},\ d_{i+2,j+1} = -\frac{R}{2}\frac{i(i+j+1)(i+j+2)(i+j+3)}{(2i+3)(2i+5)},$$

$$d_{i-1,j} = \beta\frac{(i+1)(i-j)}{(2i-1)},\ d_{i+1,j} = -\beta\frac{i(i+j+1)}{(2i+3)},$$

$$d_{i-2,j} = 2\gamma\frac{(i+1)(i-j)(i-j-1)}{(2i-1)(2i-3)},\ d_{i,j} = -2\gamma\left[1 + \frac{(i-2)(i+j)(i-j)}{(2i-1)(2i+1)} - \frac{(i+3)(i-j+1)(i+j+1)}{(2i+1)(2i+3)}\right]$$

and

$$d_{i+2,j} = -2\gamma\frac{i(i+j+1)(i+j+2)}{(2i+3)(2i+5)}.$$

Here, in the special case when $j=1$, we must double the terms of $K_{m,j-l}^{k-l,l}$ for $m = i,i \pm 2$ in Eq. (3). The coefficients K_{ij}^{k0} which describe the state before the application of an electric field satisfy next recurrent relation instead of Eq. (3).

$$i(i+1)K_{ij}^{k0} = d_{i,j-1}K_{i,j-1}^{k-1,0} + d_{i,j+1}K_{i,j+1}^{k-1,0} + d_{i-2,j-1}K_{i-2,j-1}^{k-1,0} + d_{i-2,j+1}K_{i-2,j+1}^{k-1,0} + d_{i+2,j-1}K_{i+2,j-1}^{k-1,0}$$
$$+ d_{i+2,j+1}K_{i+2,j+1}^{k-1,0}. \quad (4)$$

When $\alpha = 0$, the angular distribution function is a constant, $1/4\pi$. This means that $K_{00}^{00} = 1/4\pi$ and $K_{ij}^{00} = 0$ ($i > 0$ or $j > 0$). Using this initial condition, we can determine coefficients K_{ij}^{k0} from Eq. (4) as shown in a previous paper [6]. Moreover, these coefficients K_{ij}^{k0} and Eq. (3) make possible the determination of the coefficients K_{ij}^{k1}, the coefficients K_{ij}^{k2} and so on, recurrently. These calculation up to the order α^3 can be done by use of the computer software REDUCE although these are rather complicated. Some of the coefficients K_{ij}^{kl} are zero and the others except for K_{ij}^{k0} depend on the electric field

2.2. *The distribution function under a low alternating electric field*

The diffusion equation when an alternating electric field is applied to a solution, is denoted by

$$\left(\frac{1}{\Theta}\frac{\partial}{\partial t} - D\right)F = EP'F + E^2I'F + \alpha SF, \quad (5)$$

where operators P' and I' are equal to P/E and I/E^2. This expression and the operators are all same as those in a previous paper [6]. The difference is that the electric field E is not constant. It is expressed by

$$E = E_0 \sin \omega t. \quad (6)$$

Further, the distribution function is expanded as follows;

$$F = \Sigma\Sigma\Sigma\Sigma\, L_{ij}^{kl}\alpha^k E_0^l P_i^j \cos j\phi. \quad (7)$$

The recurrence relation we obtained is expressed by,

$$\frac{1}{\Theta}\frac{\mathrm{d}L_{ij}^{kl}}{\mathrm{d}t}+i(i+1)L_{ij}^{kl}$$
$$=d_{i,j-1}L_{i,j-1}^{k-1,l}+d_{i,j+1}L_{i,j+1}^{k-1,l}+d_{i-2,j-1}L_{i-2,j-1}^{k-1,l}+d_{i-2,j+1}L_{i-2,j+1}^{k-1,l}+d_{i+2,j-1}L_{i+2,j-1}^{k-1,l}$$
$$+d_{i+2,j+1}L_{i+2,j+1}^{k-1,l}+\left(d_{i-1,j}L_{i-1,j}^{k,l-1}+d_{i+1,j}L_{i+1,j}^{k,l-1}\right)\sin\omega t$$
$$+\left(d_{i-2,j}L_{i-2,j}^{k,l-2}+d_{i,j}L_{i,j}^{k,l-2}+d_{i+2,j}L_{i+2,j}^{k,l-2}\right)\sin^2\omega t. \quad (8)$$

The coefficients d_{nj} ($n=i$, $i\pm1$, $i\pm2$) which are obtained by replacing β and γ in d_{nj} ($n=i$, $i\pm1$, $i\pm2$) of Eq. (3) with $b(=\mu'/kT)$ and $c(=(\alpha_1-\alpha_2)/2kT)$ are all the same as those in a previous paper [6]. Coefficients L_{ij}^{kl} are calculated recurrently although they are rather complicated. Some of the coefficients L_{ij}^{kl} are zero and the others except for L_{ij}^{k0} depend on the frequency ω and time.

2.3. Birefringence and extinction angle

The refractive index n of a solution is expressed by a matrix with nine components

$$n^2=\begin{bmatrix} n_{xx}^2 & n_{xy}^2 & n_{xz}^2 \\ n_{yx}^2 & n_{yy}^2 & n_{yz}^2 \\ n_{zx}^2 & n_{zy}^2 & n_{zz}^2 \end{bmatrix}. \quad (9)$$

The birefringence Δn, the difference in the refractive indices parallel and perpendicular to the main axis of the refractive index ellipsoid, and the extinction angle χ are expressed by

$$\Delta n=\frac{1}{2n}\left\{\left(n_{zz}^2-n_{xx}^2\right)^2+\left(2n_{zx}^2\right)^2\right\}^{1/2}, \quad (10)$$

$$\cot 2\chi=-\left(n_{zz}^2-n_{xx}^2\right)/2n_{zx}^2. \quad (11)$$

Each component in Eq. (9) is calculated from the angular distribution function F and the relations obtained by Peterlin and Stuart [17]. Then two terms in Eqs. (10) and (11), $n_{zz}^2-n_{xx}^2$ and n_{zx}^2, become in the initial period after applying a rectangular electric field.

$$n_{zz}^2-n_{xx}^2=\frac{16}{5}\pi^2C_v(g_1-g_2)\Sigma\Sigma\,\alpha^k(\Theta t)^l\left(K_{20}^{kl}-2\,K_{22}^{kl}\right) \quad (12)$$

and

$$n_{xz}^2=n_{zx}^2=\frac{16}{5}\pi^2C_v(g_1-g_2)\Sigma\Sigma\alpha^k(\Theta t)^lK_{21}^{kl}, \quad (13)$$

where C_v is the volume concentration of solute and (g_1-g_2) is the optical anisotropy factor. For an alternating electric field these are expressed by,

$$n_{zz}^2-n_{xx}^2=\frac{16}{5}\pi^2C_v(g_1-g_2)\Sigma\Sigma\,\alpha^kE_0^l\left(L_{20}^{kl}-2L_{22}^{kl}\right) \quad (14)$$

and

$$n_{xz}^2=n_{zx}^2=\frac{16}{5}\pi^2C_v(g_1-g_2)\Sigma\Sigma\alpha^kE_0^lL_{21}^{kl}. \quad (15)$$

Therefore, it is easy to obtain the expressions for the birefrigence and the extinction angle from Eqs. (10) and (11). However, it is not easy to observe them directly. As shown in a previous paper [6], instead of these quantities two transmitted light intensities ΔI_{45} and ΔI_0 can be easily observed. ΔI_{45} is that when the polarizer is at 45° with respect to the electric field and the analyzer is at 90° with respect to the polarizer. ΔI_0 is that when the polarizer is at 0°. Moreover, these have been expressed by $(\Delta I_{45}) = I_0(\pi l/\lambda)^2(n_{zz}^2 - n_{xx}^2)^2/4n^2$ and $(\Delta I_0) = I_0(\pi l/\lambda)^2\ (2n_{zx}^2)^2/4n^2$, where the retardation of light is assumed to be very small compared with unity. I_0 is the intensity of light when the analyzer is set parallel to the polarizer. If $Y_{45}(\Theta t)$ and $Y_0(\Theta t)$ are defined by $Y_{45}(\Theta t) = \pm(\lambda/\pi l)(\Delta I_{45}/I_0)^{1/2}$ and $Y_0(\Theta t) = \pm(\lambda/\pi l)(\Delta I_0/I_0)^{1/2}$ and if their signs are suitably selected, they are proportional to $n_{zz}^2 - n_{xx}^2$ and n_{zx}^2, respectively. That is,

$$Y_{45}(\Theta t) = \frac{n_{zz}^2 - n_{xx}^2}{2n} \tag{16}$$

and

$$Y_0(\Theta t) = \frac{n_{zx}^2}{n}. \tag{17}$$

3. Results

The initial condition in the build-up process corresponds to the steady state distribution under a shear flow. Its approximate solution up to α^4 has been obtained from Eq. (4) and some coefficients K_{20}^{k0}, K_{22}^{k0}, and K_{21}^{k0} which relate with the birefringence and extinction angle have been shown in a previous paper [6]. Using the initial condition, we can calculate the coefficients (K_{ij}^{kl}) from Eq. (3). The terms up to $(\Theta t)^2$ and α^3 are shown in Table 1 and other terms to a higher order are presented in Appendix A. The terms, K_{20}^{0l} $(l = 1,2,...)$, which are related with the electric birefringence, coincide with those obtained by Nishinari et al. [7]. Using coefficients of K_{20}^{kl}, K_{22}^{kl}, and K_{21}^{kl}, we can obtain $Y_{45}(\Theta t)$ and $Y_0(\Theta t)$ for the build-up from Eqs. (16) and (17). Let us denote them by $Y_{45}^B(\Theta t)$ and $Y_0^B(\Theta t)$ as follows;

$$Y_{45}^B(\Theta t) = \frac{2\pi C_v(g_1 - g_2)}{15n}\left[Q_0 + Q_1(\Theta t) + Q_2(\Theta t)^2 + \cdots\right] \tag{18}$$

and

$$Y_0^B(\Theta t) = \frac{2\pi C_v(g_1 - g_2)}{15n}\left[G_0 + G_1(\Theta t) + G_2(\Theta t)^2 + \cdots\right]. \tag{19}$$

The coefficients Q_0, Q_1, Q_2 in Eq. (18) and G_0, G_1, G_2 in Eq. (19) for the build-up process are respectively expressed by,

$$Q_0 = -\frac{1}{6}\alpha^2 R\left[1 - \frac{1}{36}\alpha^2\left(\frac{11}{35}R^2 + 1\right) + \ldots\right], \tag{20}$$

$$Q_1 = \gamma\left[12 + \frac{1}{21}\alpha^2 R\left(\frac{7}{5}R - 1\right) - \frac{1}{252}\alpha^4 R\left(\frac{23}{325}R^3 - \frac{98}{825}R^2 + \frac{59}{75}R - \frac{1}{3}\right)\right], \tag{21}$$

$$Q_2 = 6(\beta^2 - 6\gamma) + \frac{24}{7}\gamma^2 - \alpha^2 R\left[\frac{1}{4}\beta^2\left(\frac{1}{5}R - \frac{17}{21}\right) + \frac{71}{105}\gamma R - \frac{2}{21}\gamma^2\left(\frac{1}{55}R + \frac{5}{3}\right)\right], \tag{22}$$

$$G_0 = \alpha R\left[1 - \frac{1}{36}\alpha^2\left(\frac{3}{35}R^2 + 1\right) + \dots\right], \tag{23}$$

$$G_1 = \frac{1}{7}\alpha\gamma R\left[2 - \frac{1}{10}\alpha^2\left(\frac{1}{11}R^2 - \frac{8}{9}R + \frac{5}{9}\right)\right], \tag{24}$$

$$G_2 = \alpha R\left\{\frac{6\gamma}{R} - \frac{17}{14}\beta^2 - \frac{22}{21}\gamma^2 + \frac{1}{21}\alpha^2\left[\beta^2\left(\frac{31}{440}R^2 - \frac{1}{5}R + \frac{17}{24}\right) - \gamma R\left(\frac{1}{11}R + \frac{29}{15}\right)\right.\right.$$
$$\left.\left. + \frac{2}{3}\gamma^2\left(\frac{59}{2860}R^2 + \frac{8}{55}R + \frac{11}{12}\right)\right]\right\}. \tag{25}$$

Their initial slopes (Q_1 and G_1) are proportional to γ.

For low alternating electric fields, $Y_{45}(\Theta t)$ defined by Eq. (16) becomes

$$Y_{45}^{A}(\Theta t) = \frac{2\pi C_v(g_1 - g_2)}{15n}\left[Q_0 + \gamma + 2\beta^2\frac{\eta^2}{\lambda_1} - \frac{3\eta}{\lambda_2}\left(\gamma + 5\beta^2\frac{\eta^2}{\lambda_1}\right)\sin(2\omega t)\right.$$
$$- \frac{3\eta^2}{\lambda_2}\left(3\gamma - \frac{1 - 6\eta^2}{\lambda_1}\beta^2\right)\cos(2\omega t) + 12\beta^2\frac{\eta^2}{\lambda_1\lambda_3}(4\eta\sin\omega t - \cos\omega t)e^{-2\Theta t}$$
$$\left. - \frac{1}{\lambda_2}\left(\gamma - 7\beta^2\frac{\eta^2}{\lambda_3}\right)e^{-6\Theta t}\right]. \tag{26}$$

where $\eta = \Theta/\omega$, $\lambda_1 = 1 + 4\eta^2$, $\lambda_2 = 1 + 9\eta^2$, and $\lambda_3 = 1 + 16\eta^2$. Moreover, γ and β in this equation mean $(\alpha_1 - \alpha_2)E_0^2/2kT$ and $\mu' E_0/kT$. All terms in this equation except for the hydrodynamic term Q_0 coincides

Table 1
Coefficients $4\pi K_{ij}^{kl}$ in low order terms with respect to reduced time $\tau(=\Theta t)$

	τ^0 $(l=0)$	τ^1 $(l=1)$	$\tau^2 (l=2)$
$4\pi K_{20}^{0l}$		4γ	$2(\beta_2 - 6\gamma) + \frac{8}{7}\gamma^2$
$4\pi K_{21}^{1l}$	$\frac{1}{6}R$	$\frac{1}{21}\gamma R$	$\gamma - \frac{17}{84}\beta^2 R - \frac{11}{63}\gamma^2 R$
$4\pi K_{20}^{2l}$	$\frac{1}{24}R(\frac{1}{7}R - 1)$	$\frac{1}{42}\gamma R(\frac{3}{5}R - 1)$	$-\frac{1}{21}R\left[\frac{5}{4}\beta^2\left(\frac{7}{25}R - 1\right) + \frac{3}{4}\gamma\left(\frac{73}{15}R - 1\right) + \gamma^2\left(\frac{1}{55}R - 1\right)\right]$
$4\pi K_{22}^{2l}$	$\frac{1}{144}R(\frac{3}{7}R + 1)$	$-\frac{1}{252}\gamma R(R + 1)$	$R\left[\frac{1}{56}\left(\frac{13}{9}R + 1\right)\gamma - \frac{1}{252}\beta^2 - \frac{1}{378}\gamma^2\left(\frac{3}{11}R + 1\right)\right]$
$4\pi K_{21}^{3l}$	$-\frac{1}{216}R(\frac{3}{35}R^2 + 1)$	$-\frac{1}{3780}\gamma R(\frac{9}{11}R^2 - 8R + 5)$	$\frac{1}{63}R\left[\frac{1}{2}\beta^2\left(\frac{31}{440}R^2 - \frac{1}{5}R + \frac{17}{24}\right) + \frac{1}{3}\gamma^2\left(\frac{59}{2860}R^2 + \frac{8}{55}R + \frac{11}{12}\right) - \frac{1}{2}\gamma R\left(\frac{1}{11}R + \frac{29}{15}\right)\right]$

with the expression for electric birefringence obtained by Ogawa et al. [13]. On the other hand, $Y_0(\Theta t)$ at low fields is given by

$$Y_0^A(\Theta t) = \frac{2\pi C_v(g_1 - g_2)}{15n}\alpha\left[G_0/\alpha + H_0 H_{1s}\sin(2\omega t) + H_{1c}\cos(2\omega t)\right.$$
$$\left. + (H_{2s}\sin\omega t + H_{2c}\cos\omega t)e^{-2\Theta t} + H_3 e^{-6\Theta t} + (H_{4s}\sin\omega t + H_{4c}\cos\omega t)e^{-12\Theta t}\right], \quad (27)$$

where coefficients of H_0, H_{1s}, ... and H_{4c} are shown in Appendix B. $Y_{45}^A(\Theta t)$ and $Y_0^A(\Theta t)$ mean $Y_{45}(\Theta t)$ and $Y_0(\Theta t)$ for low alternating electric fields.

4. Discussion

Unfortunately, the diffusion equation at arbitrary hydrodynamic field strength cannot be solved. Therefore, although the expressions of $Y_{45}^B(\Theta t)$ and $Y_0^B(\Theta t)$ in the initial period of build-up process are satisfied at arbitrary electric fields, they are limited to low hydrodynamic fields. In this condition, the main term of $Y_{45}^B(\Theta t) - Y_{45}^B(0)$ is the same as the term of electric birefringence. Hence, the function of $Y_{45}^B(\Theta t) - Y_{45}^B(0)$ in the initial period is almost independent of the hydrodynamic field or the axial ratio of a particle as shown in Fig. 2.

On the other hand, the initial slope of $Y_0^B(\Theta t)$ has the factor made up of the product between the electric parameter γ, the hydrodynamic parameter α and R. If γ and α are fixed, the initial slope is proportional to the value R. Hence, the build-up is strongly dependent of the axial ratio although it is not sensitive to low and high

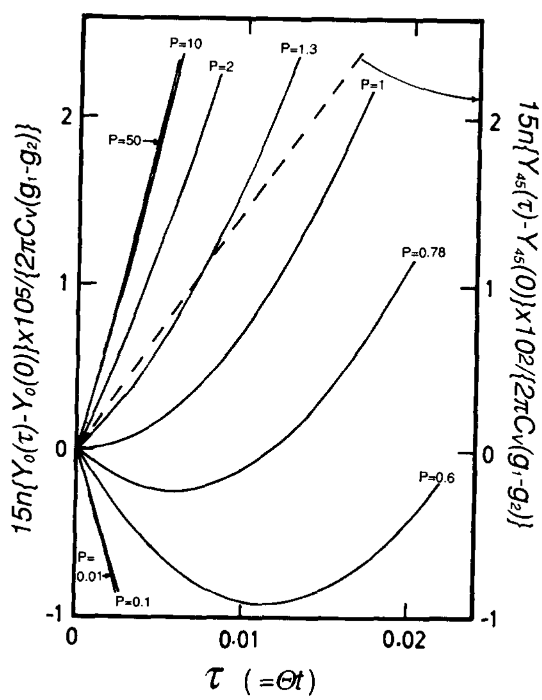

Fig. 2. Build-up curves of $Y_0^B(\Theta t)$ and $Y_{45}^B(\Theta t)$ of particles with various axial ratios(p) vs. reduced time $\tau(=\Theta t)$ under the fields; $\beta^2 + 2\gamma = 0.5(\beta^2/2\gamma = 1)$ and $\alpha = 0.1$. The broken line means the build-up of $Y_{45}^B(\Theta t)$, which is almost independent of the axial ratio.

axial ratios as shown in Fig. 2. This means that the build-up of $Y_0^B(\Theta t)$ provides us with information about the axial ratio of the solute particle. For instance, at low hydrodynamic fields, Eqs. (20), (21), (23), and (24) become respectively, $Q_0 \approx -R\alpha^2/6$, $G_0 \approx \alpha R$, $Q_1 \approx 12\gamma$, and $G_1 \approx 2\alpha\gamma R/7$. Therefore, the values of α, R, and γ, are all then obtained by following relations,

$$\alpha = -6\frac{Q_0}{G_0} = -6\frac{Y_{45}^B(0)}{Y_0^B(0)}, \tag{28}$$

$$\gamma = \frac{7G_1}{2G_0} = \frac{7Y_0^{B'}(0)}{2Y_0^B(0)}, \tag{29}$$

and

$$R = -7\frac{G_0G_1}{Q_0Q_1} = -7\frac{Y_0^B(0)Y_0^{B'}(0)}{Y_{45}^B(0)Y_{45}^{B'}(0)}. \tag{30}$$

Moreover using Eqs. (28), (29), and (30) we can calculate the optical anisotropy factor $(g_1 - g_2)$ from the following relation.

$$\frac{2}{15}\pi C_v(g_1 - g_2) = \frac{1}{42}Y_0^B(0)\frac{Q_1}{G_1} = \frac{1}{42}Y_0^B(0)\frac{Y_{45}^{B'}(0)}{Y_0^{B'}(0)} \tag{31}$$

$Y_0^{B\prime}(0)$ and $Y_{45}^{B\prime}(0)$) in these relations means the derivatives of $Y_0^B(\Theta t)$ and $Y_{45}^B(\Theta t)$ at $\Theta t = 0$. In practical, it is necessary to know the rotational diffusion coefficient in order to change time to reduced time.

When the frequency of alternating electric field is enough high, $\eta(=\Theta/\omega)$ is negligible small. Therefore, Eqs. (26) and (27) reduce to the following relations which are shown up to the first order of η.

$$Y_{45}^A(\Theta t) = \frac{2}{15n}\pi C_v(g_1 - g_2)\left\{-\frac{1}{6}R\alpha^2 + \gamma[\Delta_B(t)]_{b=0} - 3\gamma\eta\sin(2\omega t)\right\} \tag{32}$$

and

$$Y_0^A(\Theta t) = \frac{2}{15n}\pi C_v(g_1 - g_2)\alpha\left\{R - \frac{1}{36}R\alpha^2\left(\frac{3}{35}R^2 + 1\right) + \frac{1}{6}\gamma\left(\frac{2}{7}R + 1\right)[\Gamma_B(t)]_{b=0} -3\frac{1}{14}\gamma R\eta\sin(2\omega t)\right\}, \tag{33}$$

where

$$[\Delta_B(t)]_{b=0} = 1 - e^{-6\Theta t} \text{ and } [\Gamma_B(t)]_{b=0} = 1 - \left(1 + \frac{R+7}{2R+7}6\Theta t\right)e^{-6\Theta t}.$$

$[\Delta_B(t)]_{b=0}$ and $[\Gamma_B(t)]_{b=0}$ means the expression of $\Delta_B(t)$ and $\Gamma_B(t)$ when the permanent dipole moment is neglected. Their coefficients are half of those for a low rectangular electric field. The sign of the last term in Eq. (33) directly depend on that of R which is negative for a oblate ellipsoid and positive for a prolate ellipsoid.

Theoretically, it is expected that parameters of $\alpha(=G/\Theta)$, γ, R, and $(g_1 - g_2)$ can be determined from Eqs. (28), (29), (30) and (31). From the values of Θ and R, we can determine the dimension of axially symmetric solute particle or associated particle. Moreover, from the parameters of γ and $(g_1 - g_2)$, we can make sure how the solute particle is arrayed by an electric field. Therefore, as a next step, it is necessary and important to check how precisely they can be experimentally determined. Moreover, we should find out if Eqs.

(32) and (33) for an alternating electric field with high frequency are convenient to determine these parameters. Hence, experimental discussions for these theoretical results should be done. We are trying to do it and we will publish the results elsewhere.

Appendix A. Coefficients K_{ij}^{kl} which relate to the birefringence and the extinction angle in the build-up process

$$4\pi K_{21}^{13} = \frac{1}{2}\beta^2 + \frac{125}{126}R\beta^2 - 4\gamma\left(1 + \frac{1}{14}R\right) + \frac{2}{7}\gamma^2\left(1 + \frac{143}{27}R\right) - \frac{5}{54}R\beta^2\gamma - \frac{2}{33}R\gamma^3$$

$$4\pi K_{20}^{03} = 8\left\{\left(3\gamma - \frac{2}{3}\beta^2\right) - \frac{1}{7}\gamma\left(4\gamma + \frac{5}{3}\beta^2\right) - \frac{4}{21}\gamma^3\right\}$$

$$4\pi K_{20}^{23} = \frac{1}{2}\gamma\left(\frac{619}{315}R^2 - 1\right) - \frac{1}{126}R\gamma^2\left(23 + \frac{281}{55}R\right) + \frac{4}{693}R\gamma^3\left(5 - \frac{227}{65}R\right) - \frac{1}{24}R\beta^2\left(\frac{5}{3} + \frac{61}{35}R\right)$$
$$+ \frac{1}{21}R\gamma\beta^2\left(1 - \frac{31}{33}R\right)$$

$$4\pi K_{22}^{23} = \frac{1}{12}\gamma\left(1 - \frac{79}{63}R^2\right) + \frac{1}{112}R\beta^2\left(\frac{1}{27}R - 1\right) + \frac{1}{756}R\gamma^2\left(\frac{5}{11}R - \frac{23}{3}\right) + \frac{1}{18}R\beta^2\gamma\left(\frac{1}{11}R + \frac{1}{63}\right)$$
$$+ \frac{2}{2079}R\gamma^3\left(1 + \frac{37}{13}R\right).$$

Appendix B. Coefficients in Eq. (27)

$$H_0 = \frac{1}{6}\gamma\left(\frac{2}{7}R + 1\right) - \frac{1}{6}\beta^2\frac{\eta^2}{\lambda_1^2}\left[1 - 20\eta^2 + \frac{6}{7\lambda_5}R(11 + 536\eta^2 - 384\eta^4)\right]$$

$$H_{1s} = -\frac{1}{2}\gamma\frac{\eta}{\lambda_2^2}\left[\frac{1}{7}R + 18\left(\frac{3}{14}R + 1\right)\eta^2\right]$$
$$+ \beta^2\frac{\eta^3}{\lambda_1^2\lambda_2^2}\left[3(1 - 12\eta^2 - 114\eta^4) + \frac{1}{28\lambda_5}R(193 + 13489\eta^2 + 54828\eta^4 - 336960\eta^6)\right]$$

$$H_{1c} = \frac{3}{2}\gamma\frac{\eta^2}{\lambda_2^2}\left[1 - 9\eta^2\left(\frac{2}{7}R + 1\right)\right] + \beta^2\frac{\eta^2}{\lambda_1^2\lambda_2^2}\left[\frac{15}{2}\eta^2(3 + 13\eta^2 - 36\eta^4)\right.$$
$$\left. - \frac{1}{28\lambda_5}R(17 + 1037\eta^2 - 28704\eta^4 - 275616\eta^6 + 124416\eta^8)\right]$$

$$H_{2s} = 2\beta^2 \frac{\eta^3}{\lambda_1 \lambda_3} \left\{ 12\Theta t \left(\frac{3}{5} R + 1 \right) - \frac{1}{\lambda_1 \lambda_3} \left[3(1 - 28\eta^2 - 320\eta^4) + \frac{1}{175} R(301 + 6260\eta^2 - 40256\eta^4) \right] \right\}$$

$$H_{2c} = -2\beta^2 \frac{\eta^2}{\lambda_1 \lambda_3} \left\{ 3\Theta t \left(\frac{3}{5} R + 1 \right) + \frac{1}{\lambda_1 \lambda_3} \left[36(1 + 8\eta^2) - \frac{1}{350} R(233 + 4780\eta^2 - 14848\eta^4) \right] \right\}$$

$$H_3 = -\gamma \frac{1}{\lambda_2} \left\{ \Theta t \left(\frac{1}{7} R + 1 \right) + \frac{1}{6\lambda_2} \left[1 + 27\eta^2 + \frac{2}{7} R(1 + 18\eta^2) \right] \right\} + \beta^2 \frac{\eta^2}{\lambda_2 \lambda_3} \left\{ 7\Theta t \left(\frac{1}{7} R + 1 \right) + \frac{1}{6\lambda_2 \lambda_3} \left[(1 + 319\eta^2 + 3672\eta^4) - \frac{3}{14\lambda_4} R(7 + 743\eta^2 + 17868\eta^4 + 89856\eta^6) \right] \right\}$$

$$H_{4s} = \frac{1152}{175} R \beta^2 \frac{\eta^3}{\lambda_4 \lambda_5}$$

$$H_{4c} = \frac{192}{175} R \beta^2 \frac{\eta^2}{\lambda_4 \lambda_5}$$

where $\eta = \Theta/\omega$, $\lambda_1 = 1 + 4\eta^2$, $\lambda_2 = 1 + 9\eta^2$, $\lambda_3 = 1 + 16\eta^2$. $\lambda_4 = 1 + 36\eta^2$, and $\lambda_5 = 1 + 144\eta^2$.

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