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Optical Saturation of Electrical and Optical Anisotropy Induced in Suspensions of Asymmetric Rigid Particles

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Asymmetric particles suspended in an isotropic medium are apt to undergo complete ordering, leading to their alignment in the oscillation direction of the electric vector of a linearly polarized laser beam or in the propagation direction of a circularly polarized one. The resulting state of "optical saturation" causes the suspension to become strongly birefringent and, simultaneously, electrically anisotropic. Measurements of these two effects are proposed as a method permitting direct determinations of the electric and optical anisotropies of rigid particles. Simple formulas are derived and lead to numerical evaluations proving such measurements to be readily feasible in suspensions of particles smaller than 1000 Å if one uses light from a high-power pulse ruby laser, whereas total optical orientation of large biomacromolecules in suspension can be achieved with light from a high-power continuously operating gas laser. Optical saturation of the low-frequency dielectric constant can moreover serve for determining the anisotropy of electric dipole polarizability of particles and their relaxation times.

INTRODUCTION

In recent years, more and more attention is being given to the electric and optical properties of particles, especially biomacromolecules, when in suspension in other media. The optical and electric anisotropies of various rigid biomolecules were successfully determined by methods involving their orientation in external electric fields (1, 2), such as measurements of Kerr's electrooptic effect (3–6) and measurements of light scattering in the presence of an electric field (7–9). Moreover, the optical anisotropy of particles is accessible to determination by purely optical methods, involving orientation in the electric field of an intense laser beam (10) and, particularly, by the study of optical saturation in laser light scattering (11).

It is our aim to propose another method of determining the sign and value of the electric and optical anisotropy of a particle by employing the optical saturation of anisotropy of the dielectric constant and the saturation of optical birefringence. Owing to the laser technique now generally available in laboratories, this method based on optical saturation and permitting the electrode-less application of very strong electric fields to the solution under investigation will present certain advantages over the hitherto used method of electric saturation (4–6, 9). In this way, undesirable phenomena such as electrostriction, linear electrophoretic effect, and dielectric breakdown which in general accompany the application of strong d-c electric fields are eliminated. The earliest investigations by a laser technique, carried out by this department (12), have already revealed a high degree of optical orientation of gold particles suspended in water as a result of the optical anisotropy of these par-

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ticles (10, 13). All in all, the method of optical orientation of particles promises to prove easy and convenient in experimental work and to be a lavish source of information concerning their electrooptical properties.

THEORETICAL

We consider rigid ellipsoidal particles, their geometrical axes coinciding with the principal 1, 2, 3-axes, along which the permanent electric dipole moment components μ_1, μ_2, μ_3 lie. The a-c electric field[2] $\mathbf{F}_\omega = \mathbf{F}_0 e^{i\omega t}$ (oscillating at circular frequency ω) acting upon the medium causes a deformation of the electric charge distribution of the particles and a reorientation of their permanent electric dipoles. Provided the electric field $\mathbf{F}_\omega$ is not excessive, the deformational polarization induced in the medium at frequency ω can be written in the well-known linear form (2, 3):

$$\mathbf{P}_\omega^{\text{def}} = \frac{N}{3}(\alpha_1{}^\omega + \alpha_2{}^\omega + \alpha_3{}^\omega)\mathbf{F}_\omega, \qquad [1]$$

with N the number of particles per unit volume and $\alpha_1{}^\omega$, $\alpha_2{}^\omega$, $\alpha_3{}^\omega$ the three principal electric polarizabilities of the particle (in general, complex quantities depending on ω).

For the electric polarization due to reorientation of permanent dipoles, the Langevin-Debye theory yields (14)

$$\mathbf{P}_\omega^{\text{reor}} = \frac{N}{3kT}\left(\frac{\mu_1{}^2}{1 + i\omega\tau_1} + \frac{\mu_2{}^2}{1 + i\omega\tau_2} + \frac{\mu_3{}^2}{1 + i\omega\tau_3}\right)\mathbf{F}_\omega, \qquad [2]$$

τ_1, τ_2, τ_3 denoting relaxation times of dipoles along the principal axes 1, 2, 3 of a particle.

We now consider the situation when the particles are in suspension in a different, isotropic medium. The suspension is assumed to be so dilute as to rule out direct interactions between the particles, and the solvent is assumed to leave unaffected their electric properties. In a weak a-c electric field $\mathbf{F}$, by formulas [1] and [2], the dielectric permittivity $\epsilon_0{}^\omega$ of the suspension as a whole is an isotropic quantity and does not depend on the field strength $\mathbf{F}_0$ but rather on the oscillation frequency ω of the field. If, however, the suspension is subjected to illumination with an intense laser beam, its electric permittivity undergoes nonlinear variations which are anisotropic (15): $\Delta\epsilon_{\sigma\tau}^\omega = \epsilon_{\sigma\tau}^\omega - \epsilon_0{}^\omega\delta_{\sigma\tau}$, $\epsilon_{\sigma\tau}^\omega$ being the tensor of electric permittivity of the suspension measured with a weak a-c electric field at frequency ω in the presence of the laser light. In order to simplify our calculations, we assume the particles to have the shape of rotational ellipsoids, so that the polarizability and dipole moment components now are $\alpha_3 = \alpha_\parallel$ and $\mu_3 = \mu_\parallel$ along the symmetry axis, whereas $\alpha_\perp = \alpha_1 = \alpha_2$ and $\mu_\perp = \mu_1 = \mu_2$ are perpendicular thereto. Restricting further considerations to variations due to orientation of the ellipsoids of electronic polarizability of the particles in the electric field $\mathbf{E}^L = \mathbf{E}^0 \cos\omega_L t$ of the laser beam (frequency ω_L), we have (see Appendix):

$$\Delta\epsilon_{\sigma\tau}^\omega = (S_\alpha{}^\omega + S_\mu{}^\omega)\langle c_{\sigma 3}c_{\tau 3} - \tfrac{1}{3}\delta_{\sigma\tau}\rangle_I{}^L, \qquad [3]$$

$c_{\sigma 3}$ and $c_{\tau 3}$ denoting cosines of angles between the axes σ and τ of laboratory coordinates and the symmetry 3-axis of the particle; $\delta_{\sigma\tau}$ is Kronecker's unit tensor. The constants $S_\alpha{}^\omega$ and $S_\mu{}^\omega$, defining the electric properties of the suspension and its thermodynamical state, are of the following form in the case of axially symmetric particles:

$$S_\alpha{}^\omega = 4\pi\frac{cN_A}{M}(\alpha_\parallel{}^\omega - \alpha_\perp{}^\omega); \qquad [4]$$

$$S_\mu{}^\omega = 4\pi\frac{cN_A}{MkT}\left(\frac{\mu_\parallel{}^2}{1 + i\omega\tau_\parallel} - \frac{\mu_\perp{}^2}{1 + i\omega\tau_\perp}\right); \qquad [5]$$

[2] Since this paper deals with dilute solutions of particles which are much larger than the molecules of the solvent, the mean macroscopic field existing within the medium does not differ from the field really acting on the particle, shape-dependent depolarization factors of the field being comprised in the quantities α_s and μ_s.

with c the concentration in grams per cubic centimeter, M the molecular weight of the substance in suspension, and N_A Avogadro's number.

Statistical averaging in the expression [3] indicated by the symbol $\langle\ \rangle_{IL}$ is performed with Boltzmann's distribution function in the presence of laser light of intensity I^L:

$$f(\Omega, I_L) = \frac{\exp\left\{-\frac{u(\Omega, I^L)}{kT}\right\}}{\int \exp\left\{-\frac{u(\Omega, I^L)}{kT}\right\} d\Omega}, \quad [6]$$

where $u(\Omega, I^L)$, the potential energy in the electric field of the laser wave, depends on the orientation Ω of the axially symmetric particle and is given as follows (10):

$$u(\Omega, I^L) = u_0 - \tfrac{1}{2}(\alpha_{\parallel}^{\omega L} - \alpha_{\perp}^{\omega L}) c_{\sigma 3} c_{\tau 3} \langle E_\sigma^L E_\tau^L \rangle_t, \quad [7]$$

the symbol $\langle\ \rangle_t$ standing for time-averaging over the period of oscillations of the electric field of the laser wave. Summation over recurring indices σ and τ is implicit.

We chose the linearly polarized laser beam to propagate through the suspension along the laboratory z-axis with electric vector $\mathbf{E}^L$ oscillating along the x-axis. With the symmetry 3-axis of the particle subtending the angle Θ with the laboratory x-axis, we write the directional cosines as follows:

$$\begin{aligned} c_{x3} &= \cos\vartheta, \\ c_{y2} &= \sin\vartheta\cos\varphi, \\ c_{z3} &= \sin\vartheta\sin\varphi, \end{aligned} \quad [8]$$

φ being the azimuth of the symmetry axis.

With [6]-[8], Eq. [3] yields the following nonvanishing components of the change in electric permittivity tensor:

$$\begin{aligned} &\Delta\epsilon_{xx}^{\omega}(I_1^L) \\ &\quad = \tfrac{2}{3}(S_\alpha^\omega + S_\mu^\omega)\Phi(\pm q_1); \\ &\Delta\epsilon_{yy}^{\omega}(I_1^L) \\ &\quad = \Delta\epsilon_{zz}^{\omega}(I_1^L) \\ &\quad = -\tfrac{1}{3}(S_\alpha^\omega + S_\mu^\omega)\Phi(\pm q_1). \end{aligned} \quad [9]$$

Above, the reorientation function is of the form (4, 5, 11):

$$\Phi(\pm q_1) = \pm \frac{3e^{\pm q_1}}{4\sqrt{q_1}\int_0^{\sqrt{q_1}} e^{\pm t^2}\, dt} \mp \frac{3}{4q_1} - \frac{1}{2}, \quad [10]$$

where q_1, the reorientation parameter of the particle in the linearly polarized laser wave of intensity $I_x^L = \langle E_x^L E_x^L \rangle_t$, is:

$$q_1 = |\alpha_{\parallel}^{\omega L} - \alpha_{\perp}^{\omega L}| I_x^L / 2kT. \quad [11]$$

The sign "+" refers to the case of cigar-shaped or rodlike particles, i.e., to positive optical anisotropy when $\alpha_{\parallel}^{\omega L} > \alpha_{\perp}^{\omega L}$, whereas the sign "−" is for disc-shaped particles, where the optical anisotropy is negative, $\alpha_{\parallel}^{\omega L} < \alpha_{\perp}^{\omega L}$. The function [10] has been tabulated for either case (4, 5) and is plotted in Fig. 1.

Let us moreover consider the situation which arises when the laser wave propagating along the z-axis is circularly polarized with electric vector amplitudes

$$E_{\pm}^L = (E_x^L \pm iE_y^L)/\sqrt{2}$$

for right and left circularly polarized waves, respectively. In order that the potential energy [7] shall not depend on the azimuth Φ, it is now convenient to use, instead of the transformation [8], one in which the angle

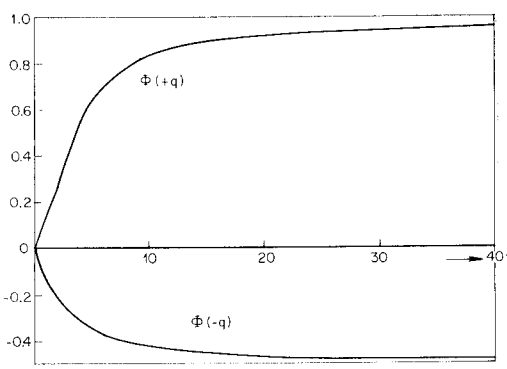

FIG. 1. Graph showing the reorientation function [10] versus the parameter q for cigar-shaped particles, $\Phi(+q)$, and disc-shaped particles, $\Phi(-q)$.

ϑ is subtended by the symmetry 3-axis of the particle and the laboratory z-axis (the propagation direction of the laser beam). By Eqs. [3], [6], and [7] we now have:

$$\begin{aligned}\Delta\epsilon_{xx}^{\omega}(I_c^{L}) &= \Delta\epsilon_{yy}^{\omega}(I_c^{L}) \\ &= -\tfrac{1}{3}(S_\alpha^{\omega} + S_\mu^{\omega})\Phi(\mp q_c), \\ \Delta\epsilon_{zz}^{\omega}(I_c^{L}) &= \tfrac{2}{3}(S_\alpha^{\omega} + S_\mu^{\omega})\Phi(\mp q_c),\end{aligned} \quad [12]$$

where the reorientation function $\Phi(\mp q_c)$ is of the form [10] on inverting the signs $\pm$ to $\mp$ and on replacing the reorientation parameter [11] by

$$q_c = |\alpha_{\parallel}^{\omega L} - \alpha_{\perp}^{\omega L}|(I_-^{L} + I_+^{L})/4\,kT, \quad [13]$$

a reorientation parameter of the particle in the circularly polarized laser field of intensity $I_c^{L} = I_-^{L} + I_+^{L}$, with $I_\pm^{L}$ denoting the intensities for the two senses of circular polarization.

APPLICATIONS AND DISCUSSION

Defining the electric anisotropy induced optically in the medium as the difference between mutually perpendicular components of the change in electric permittivity measured perpendicularly to the direction of propagation of the laser wave, we obtain in conformity with Eq. [9] for linearly polarized light:

$$\begin{aligned}\Delta\epsilon_{xx}^{\omega}(I_1) - \Delta\epsilon_{yy}^{\omega}(I_1) \\ = (S_\alpha^{\omega} + S_\mu^{\omega})\Phi(\pm q_1).\end{aligned} \quad [14]$$

On the other hand, Eqs. [12] show that circularly polarized light does not induce in the medium an electric anisotropy of the kind defined above. In the present case, anisotropy is induced only between the components $\Delta\epsilon_{xx}^{\omega}$ and $\Delta\epsilon_{yy}^{\omega}$ measured perpendicularly to the propagation direction and the component $\Delta\epsilon_{zz}^{\omega}$ measured parallel to that direction.

Equations [9] and [12] lead to the significant relation

$$\frac{\Delta\epsilon_{xx}^{\omega}(I_1^{L})}{\Delta\epsilon_{xx}^{\omega}(I_c^{L})} = -2\frac{\Phi(\pm q_1)}{\Phi(\mp q_c)} \quad [15]$$

between the absolute changes in electric permittivity of the medium caused, respectively, by linearly and circularly polarized laser light.

In the case $q_1 < 1$ when reorientation of the particles is not excessive, the reorientation function [10] can be replaced by the expansion:

$$\Phi(\pm q_1) = \pm\frac{2q_1}{15} + \frac{4q_1^{2}}{315} \mp \frac{8q_1^{3}}{4725} + \cdots \quad [16]$$

Conversely, in the limiting case of optical saturation when all the particles are aligned parallel to the electric oscillations of the light wave and the reorientation parameters [11] and [13] become very large, $q \gg 1$, we have (4, 5)

$$\Phi(+\infty) = 1 \quad \text{and} \quad \Phi(-\infty) = -\tfrac{1}{2}. \quad [17]$$

If it is taken into account that by Eqs. [11] and [13] $q_1 = 2q_c$, the ratio [15] amounts to 4 for weak reorientation described by the first term of the expansion [16], whereas by Eq. [17] for optical saturation it still amounts to 4 for cigar-shaped particles but falls to 1 for disc-shaped ones. Thus, whereas Eq. [14] permits determinations of the value of the anisotropy of polarizability, the relation [15] can be useful in determining the sign of the anisotropy and, consequently, the shape of the particle.

If the experimental setup is modified in a manner to use a probe light instead of the measuring a-c electric field, $\omega\tau$ tends to infinity and the dielectric constant [5] vanishes owing to the permanent dipoles' being unable to follow the rapidly oscillating electric field of the probe light. In this case, Eq. [14] with regard to [4] goes over into:

$$\begin{aligned}\Delta n_{xx}^{1} - \Delta n_{yy}^{1} = 2\pi\frac{cN_A}{nM} \\ \cdot(\alpha_{\parallel}^{\omega} - \alpha_{\perp}^{\omega})\Phi(\pm q_1).\end{aligned} \quad [18]$$

Equation [18] describes the optical birefringence induced in the medium by intense linearly polarized laser light, n being the refractive index independent of the light intensity. Obviously, Eq. [18] also accounts for optical saturation of birefringence and will permit determinations of the optical anisotropy of particles by analogy to the method of electric birefringence saturation measurements due to O'Konski *et al.* (4–6).

In the optical case, the relation [15] becomes:

$$\frac{\Delta n_1}{\Delta n_c} = -2\frac{\Phi(\pm q_1)}{\Phi(\mp q_c)}, \qquad [19]$$

Δn_1 and Δn_c denoting, respectively, the absolute change in refractive index induced by strong linearly polarized and circularly polarized laser light.

The expressions [9] and [12] moreover yield Havelock's relations (16) for linearly and circularly polarized laser light:

$$\frac{\Delta n^1_{xx}}{\Delta n^1_{yy}} = -2\frac{\Delta n^c_{xx}}{\Delta n^c_{yy}} = -2. \qquad [20]$$

The relaxation times of molecules lying in the 10^{-10}–10^{-12} sec range permit use of the pulse technique of giant lasers, making it possible to observe the optical Kerr effect in molecular liquids (17) where the experimental birefringence depends on the intensity I_L of the laser beam (18) in accordance with Eqs. [16] and [18].

Recent measurements of absolute changes in refractive index by Paillette (19) by a laser technique have confirmed Havelock's relations [20] and thereby have served to corroborate Langevin's theory of optical orientation of molecules (1).

As yet, no observations of optical saturation in molecular liquids are available. This is quite obviously due to the fact that the optical anisotropy of molecules is of the order of 10^{-23}, leading to a very small reorientation parameter [11] of $q_1 = 10^{-10} I_L$. In such circumstances, an extremely intense laser beam conveying a field of 10^5 esu would be required to induce optical saturation. Such fields, though generally available nowadays when giant lasers are used, cause optical breakdown in the liquid (20) before complete optical ordering of the molecules (i.e., optical saturation) is reached.

A considerable degree of ordering (alignment) can be achieved in dilute solutions of rigid macromolecules where electric saturation of optical birefringence appears easily (4–6). Obviously, when applying pulse laser technique instead of a d-c electric field for the study of polymers and colloids, one has to choose the experimental conditions such as to allow these macromolecules or particles to orient themselves during the time interval of a single light pulse. The relaxation times of proteins in water lie in the 10^{-6}–10^{-8} sec range (21, 22), and consequently high-power ruby lasers with a pulse duration of 10^{-4}–10^{-7} sec at wavelength 6943 Å and an electric field strength of at least 100 esu in the beam (or even 10^4 esu in the focused beam) will still be applicable. Assuming the optical anisotropy of proteins as being of the order of 10^{-18} cm^3, one finds an orientation parameter $q_1 = 10^{-5} I_L$, and optical saturation can be achieved with pulse laser light of intensity I_L of the order 10^5–10^6 esu. Effects of the same order of magnitude have also been obtained in colloid solutions of gold and silver particles, where strong optical orientation takes place for particles not exceeding 500 Å in size (10–13).

As the relaxation times of large biomacromolecules such as collagen, DNA, and TMV are by no means short, amounting to 10^{-2}–10^{-4} sec (6, 8), their solutions can be investigated only with continuously operating lasers of high power. The optical anisotropy of collagen is 3×10^{-15} cm^3 (6), that of TMV 3×10^{-14} cm^3 (4), and that of DNA of the order 10^{-15} cm^3 (23), whence their orientation parameter is correspondingly very large; $q_1 = (0.1 \div 0.01) I_L$. In solutions like these, full optical saturation can be arrived at when using an argon laser of high power generating continuously light of wavelengths 4880 and 5145 Å, conveying an electric field

the strength of which can amount to as much as 10 esu or, at the focus, 100 esu.

The preceding discussion shows that, in colloidal suspensions, optical saturation of the dielectric constant as well as optical saturation of optical birefringence can be observed by means of existing laser techniques. We thus are in possession of a new method of determining the sign and size of the optical and electrical anisotropies of macromolecules and colloid particles. Investigations of these new effects, combined with our knowledge of electric saturation, will make it possible not only to determine the anisotropy of particles but moreover to measure separately their optical polarizabilities parallel to the symmetry axis and perpendicular thereto, as already done for the majority of molecules (24). It may also be worth noting that, if the anisotropy of electronic polarizability implicit in the constant [4] is known, investigation of optical saturation of the low-frequency dielectric constant in accordance with Eq. [5] will permit determinations of the anisotropy of polarizability of permanent electric dipole moments of particles or their times of relaxation.

APPENDIX

Since the measuring a-c electric field **F** is not very strong, the reorientation of dipolar particles caused by it is not very considerable. We thus are justified in writing the distribution function in a linear approximation as follows (14):

$$f = f_0\left\{1 + \frac{\mu_s c_{\sigma s} F_{0\sigma} e^{i\omega t}}{kT(1 + i\omega\tau_s)}\right\} \qquad [A1]$$

with μ_s and τ_s denoting, respectively, the dipole moment component and its relaxation time along the principal axis $s = 1, 2, 3$ of the particle which subtends the angle $c_{\sigma s}$ with the laboratory σ-axis.

With regard to Eq. [A1] and the well-known relations between the electric permittivity and electric polarization, we obtain the change in electric permittivity tensor measured at frequency ω in the form:

$$\Delta\epsilon_{\sigma\tau}^{\omega} = \frac{8\pi c N_A}{3M}\left[(\beta_1{}^{\omega} - \beta_2{}^{\omega})\psi_{\sigma\tau} + \left(\beta_3{}^{\omega} - \frac{\beta_1{}^{\omega} + \beta_2{}^{\omega}}{2}\right)\Phi_{\sigma\tau}\right], \qquad [A2]$$

where we have denoted by $\beta_1{}^{\omega}$, $\beta_2{}^{\omega}$, $\beta_3{}^{\omega}$ the total electric polarizabilities along the principal axes of the particle:

$$\beta_s{}^{\omega} = \alpha_s{}^{\omega} + \frac{\mu_s{}^2}{kT(1 + i\omega\tau_s)} \qquad [A3]$$

consisting of the distortional-electronic polarizabilities $\alpha_s{}^{\omega}$ and the dipolar-orientational polarizabilities defined by the second term of [A3].

The tensors appearing in Eq. [A2]:

$$\psi_{\sigma\tau} = \tfrac{3}{4}\langle c_{\sigma 1}c_{\tau 1} - c_{\sigma 2}c_{\tau 2}\rangle, \qquad [A4]$$

$$\Phi_{\sigma\tau} = \tfrac{1}{2}\langle 3c_{\sigma 3}c_{\tau 3} - \delta_{\sigma\tau}\rangle, \qquad [A5]$$

define the reorientation of particles as due to other external factors, such as an intense d-c electric or magnetic field or the light vector of a laser beam.

In the absence of intense external fields when the orientation of particles in the suspension is quite random, unweighted averaging over all possible orientations of particles yields:

$$\langle c_{\sigma 1}c_{\tau 1}\rangle = \langle c_{\sigma 2}c_{\tau 2}\rangle = \langle c_{\sigma 3}c_{\tau 3}\rangle = \tfrac{1}{3}\delta_{\sigma\tau} \qquad [A6]$$

and, quite obviously, the orientation tensors [A4] and [A5] vanish and the electric permittivity exhibits no variation.

In the presence of orientation-producing external fields, the tensors [A4] and [A5] have in general nonvanishing components (25), causing an induced anisotropy of the suspension. We are interested here in the limiting case when the agent externally applied to the suspension is so intense as to cause all the particles to align totally in the direction of the field. Assuming the particles to possess symmetry with respect to their principal 3-axis, the first term containing the orientational tensor [A4] in Eq. [A2] vanishes (this tensor vanishes any way at saturation) and

we obtain the expression [3] in the form:

$$\Delta\epsilon_{\sigma\tau}^{\omega} = \frac{8\pi c N_A}{3M}(\beta_{\parallel}{}^{\omega} - \beta_{\perp}{}^{\omega})\Phi_{\sigma\tau}, \quad [A7]$$

since now $\beta_3{}^{\omega} = \beta_{\parallel}{}^{\omega}$ and $\beta_1{}^{\omega} = \beta_2{}^{\omega} = \beta_{\perp}{}^{\omega}$. If the field causing saturation of orientation acts, say, along the z-axis, the orientational tensor [A5] becomes:

$$\Phi_{\sigma\tau}^{p} = (3\delta_{\sigma z}\delta_{\tau z} - \delta_{\sigma\tau})/2 \quad [A8]$$

for prolate particles with their long 3-axis lying in the z-direction, or

$$\Phi_{\sigma\tau}^{o} = (3\delta_{\sigma x}\delta_{\tau x} + 3\delta_{\sigma y}\delta_{\tau y} - 2\delta_{\sigma\tau})/4 \quad [A9]$$

for oblate particles with their short symmetry axis directed parallel to the z-axis and their long axis lying in the xy-plane.

By [A8] and [A9], we have the following nonzero components:

$$\Phi_{zz}^{p} = 1, \quad \Phi_{xx}^{p} = \Phi_{yy}^{p} = -\tfrac{1}{2}, \quad [A10]$$

$$\Phi_{xx}^{o} = \Phi_{yy}^{o} = \tfrac{1}{4}, \quad \Phi_{zz}^{o} = -\tfrac{1}{2}, \quad [A11]$$

leading to the following anisotropy values at saturation:

$$\Phi_{zz}^{p} - \Phi_{xx}^{p} = \Phi_{zz}^{p} - \Phi_{yy}^{p} = \tfrac{3}{2}, \quad [A12]$$

$$\Phi_{zz}^{o} - \Phi_{xx}^{o} = \Phi_{zz}^{o} - \Phi_{yy}^{o} = -\tfrac{3}{4}. \quad [A13]$$

With regard to these results, the ratio of saturation anisotropy for prolate and oblate particles amounts to:

$$\frac{\Phi_{zz}^{p} - \Phi_{xx}^{p}}{\Phi_{zz}^{o} - \Phi_{xx}^{o}} = -2 \quad [A14]$$

irrespective of the nature of the agent inducing the anisotropy.

Let us now consider the case when reorientation of particles is due to the electric field of a laser wave. We assume that the beam is propagating along the z-axis. If the wave is plane polarized with electric oscillations along the x-axis, the distribution function [6] with regard to [7] and [8] reduces to:

$$f(\vartheta, I^L) = \frac{\exp(\pm q_1 \cos^2\vartheta)}{2\pi\int_0^{\pi}\exp(\pm q_1\cos^2\vartheta)\sin\vartheta\, d\vartheta}. \quad [A15]$$

By [8] the principal components of the reorientation tensor [A5] are now:

$$\begin{aligned}\Phi_{xx}^{1} &= \tfrac{1}{2}\langle 3c_{x3}^2 - 1\rangle_{I_1^L} \\ &= \tfrac{1}{2}\langle 3\cos^2\vartheta - 1\rangle_{I_1^L}, \\ \Phi_{yy}^{1} &= \tfrac{1}{2}\langle 3c_{y3}^2 - 1\rangle_{I_1^L} \\ &= \tfrac{1}{2}\langle 3\sin^2\vartheta\cos^2\varphi - 1\rangle_{I_1^L}, \\ \Phi_{zz}^{1} &= \tfrac{1}{2}\langle 3c_{z3}^2 - 1\rangle_{I_1^L} \\ &= \tfrac{1}{2}\langle 3\sin^2\vartheta\sin^2\varphi - 1\rangle_{I_1^L}.\end{aligned} \quad [A16]$$

Since the distribution function [A15] does not depend on the azimuth φ, it is permissible first to average the components Φ_{yy} and Φ_{zz} over all possible values of φ, thus $\langle\cos^2\varphi\rangle = \langle\sin^2\varphi\rangle = \tfrac{1}{2}$, yielding finally:

$$\Phi(\pm q_1) = \Phi_{xx}^{1} = -2\Phi_{yy}^{1} = -2\Phi_{zz}^{1}, \quad [A17]$$

where the reorientation function $\Phi(\pm q_1)$ is defined by Eq. [10].

In the case of a circularly polarized laser wave propagating along the z-axis, it is well to assume (as usual) that the symmetry axis of the particle forms an angle ϑ with the z-axis. In place of [8], we now obtain:

$$\begin{aligned}c_{x3} &= \sin\vartheta\cos\varphi, \\ c_{y3} &= \sin\vartheta\sin\varphi, \\ c_{z3} &= \cos\vartheta,\end{aligned} \quad [A18]$$

permitting us to express the energy [7] as a function of the angle only:

$$u(\vartheta, I_c{}^L) = u_0 \mp kT\, q_c \sin^2\vartheta, \quad [A19]$$

since $\langle E_x{}^L E_x{}^L\rangle_t = \langle E_y{}^L E_y{}^L\rangle_t = \tfrac{1}{4}(|\, E_+{}^L\,|^2 + |\, E_-{}^L\,|^2) = \tfrac{1}{2}(I_+{}^L + L_-{}^L)$ and $\langle E_x{}^L E_y{}^L\rangle_t = 0$. The reorientation parameter q_c is given by [13].

Inserting the energy [A19] into the distribution function [6] and resorting to [A18], we obtain the following principal components of the reorientation tensor [A5]:

$$\Phi(\mp q_c) = \Phi_{zz}^{c} = -2\Phi_{xx}^{c} = -2\Phi_{yy}^{c}. \quad [A20]$$

At this point one has to keep in mind that for particles with positive anisotropy we have to take the upper "minus" sign, whereas

particles with negative anisotropy require the lower "plus" sign. This inversion of the signs is due to the fact that in the case of circularly polarized light the particles tend to orient themselves with their symmetry axis in the direction of propagation of the light beam, which defines the optical axis of induced anisotropy of the medium.

For particles having the rotational ellipsoid symmetry, Eqs. [A2], [A17], and [A20] lead to the following relations:

$$\frac{\Delta\varepsilon_{xx}^{\omega}(I_1{}^L)}{\Delta\varepsilon_{xx}^{\omega}(I_c{}^L)} = -2\frac{\Delta\varepsilon_{yy}^{\omega}(I_1{}^L)}{\Delta\varepsilon_{yy}^{\omega}(I_c{}^L)} = 4\frac{\Delta\varepsilon_{zz}^{\omega}(I_1{}^L)}{\Delta\varepsilon_{zz}^{\omega}(I_c{}^L)}, \qquad [A21]$$

which are extensions of Eq. [15].

REFERENCES

1. LANGEVIN, P., *Radium* **7,** 249 (1910).
2. PETERLIN, A., AND STUART, H. A., *Z. Physik* **112,** 129 (1939).
3. BENOIT, H., *Ann. Phys. (Paris)* **6,** 561 (1951); BOECKEL, G., GENZLING, J. C., WEILL, G., AND BENOIT, H., *J. Chim. Phys,* 999 (1962).
4. O'KONSKI, C. T., YOSHIOKA, K., AND ORTTUNG, W. H., *J. Phys. Chem.* **63,** 1558 (1959); KRAUSE, S., AND O'KONSKI, C. T., *J. Am. Chem. Soc.* **81,** 5082 (1959).
5. SHAH, M. J., *J. Phys. Chem.* **67,** 2215 (1963).
6. YOSHIOKA, K., AND O'KONSKI, C. T., *Biopolymers* **4,** 499 (1966).
7. WIPPLER, C., AND BENOIT, H., *Makromol. Chem.* **13,** 7 (1954); WALLACH, M. L., AND BENOIT, H., *J. Polymer. Sci.* **57,** 41 (1962).
8. JENNINGS, B. R., AND JERRARD, H. G., *J. Phys. Chem.* **69,** 2817 (1965); *J. Chem. Phys.* **44,** 1291 (1966); JENNINGS, B. R., AND PLUMMER, H., *J. Colloid Interfac. Sci.* **27,** 377 (1968).
9. STOYLOV, S., *Collect. Czech. Chem. Commun.* **31,** 2866, 3052 (1966); *J. Polymer Sci.* **16,** 2435 (1967).
10. KIELICH, S., *J. Colloid Interfac. Sci.* **27,** 432 (1968); *ibid.* **28,** 214 (1968) and references therein.
11. KIELICH, S., *Appl. Phys. Lett.* **13,** 371 (1968).
12. KACZMAREK, F., *Acta Phys. Polon.* **32,** 1003 (1967).
13. KIELICH, S., *Chem. Phys. Lett.* **1,** 675 (1968).
14. PERRIN, F., *J. Phys. Radium* **5,** 497 (1937).
15. KIELICH, S., *Physica* **34,** 365, 586 (1967).
16. HAVELOCK, T. H., *Proc. Roy. Soc. (London)* **77,** 170 (1906); *ibid.* **80,** 28 (1908), cited after Langevin (1).
17. MAYER, G., AND GIRES, F., *Comp. Rend.* **258 B,** 2039 (1964); PAILLETTE, M., *ibid.* **262 B,** 264 (1966); SHIMIZU, F., *J. Phys. Soc. Jap.* **22,** 1070 (1967).
18. KIELICH, S., IEEE. J. Quantum Electronics, *QE-4,* 744 (1968); *Acta Phys. Polon.* **34,** 1093 (1968).
19. PAILLETTE, M., *Compt. Rend.* **267 B,** 29 (1968).
20. LALANNE, J. R., AND BOTHOREL, P., *Compt. Rend.* **263 B,** 693 (1966); LALANNE, J. R., *ibid.* **265 B,** 1181 (1967); DOWLEY, M. W. EISENTHAL, K. B., AND PETICOLAS, W. L., *Phys. Rev. Lett.* **18,** 531 (1967).
21. STUART, H. A., ed., "Das Makromolekül in Lösungen." Springer-Verlag, Berlin, 1953.
22. KRAUSE, S., AND O'KONSKI, C. T., *Biopolymers* **1,** 503 (1963).
23. WEILL, G., HORNICK, C., AND STOYLOV, S., *J. Chim. Phys.* **65,** 182 (1968).
24. LE FEVRE, C. G., AND LE FEVRE, R. J. W., *Rev. Pure Appl. Chem.* **5,** 261 (1955).
25. HOLCOMB, D. N., AND TINOCO, I., JR., *J. Phys. Chem.* **67,** 2691 (1963).