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The State of Polarization of Light Scattered by Anisotropic Spheroids

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Using the light scattering theory of Rayleigh–Gans, theoretical expressions were derived for the state of polarization of light scattered by anisotropic spheroids in the case of linearly polarized incident light whose electric vector is inclined by ψ to the scattering plane. The azimuth of the ellipse of the light scattered is a function of the two scattering angles, θ and ψ, only and the scattered light is linearly polarized for linearly polarized incident light. The degree of polarization of the scattered light, which is defined as the ratio of the polarized component to the intensity of the scattered light, depends on the intrinsic anisotropy, p_m; the relative refractive index of the spheroid to the solvent, m, and θ, together with the ψ angle. The degree of polarization varies from 1.0 to 0, depending strongly on p_m, p, and m. It has been suggested that the determination of the degree of polarization as a function of ψ and θ provides good information about the optically intrinsic anisotropy of the spheroid.

For most proteins and nucleoproteins in water or dilute salt solutions, the anisotropy is too small to affect the angular distribution of light scattering. Only in the case of positively birefringent and anisometric particles is there likely to be any influence of the anisotropy on the angular distribution of light scattering.[1,2] Bovine serum albumin in a native state is known to be somewhat asymmetrical and to possess an intrinsic anisotropy.[3,4] The appreciable intrinsic anisotropy parameter of bovine serum albumin has been experimentally determined.[3]

The light scattered by optically anisotropic scatterers is partially polarized and contains some unpolarized component. In the cases of optically isotropic and anisometric particles[5),6] and also optically anisotropic spheres,[7] the state of polarization of scattered light has already been calculated on the basis of the Rayleigh[8]–Gans[9] theory, which will henceforth be referred to as the Rayleigh–Gans theory of spheroids (RGS theory) in order to avoid confusion with the well-known Rayleigh–Gans (RG) theory of scattering, which involves the restrictive assumption that the refractive index of the particle is close to that of the surrounding medium. However, to the author's knowledge, no theory exists for taking into consideration the optically anisotropic effect on the light scattered by spheroids.

In the present paper, the effect of the intrinsic optical anisotropy on the state of polarization of light scattered by spheroids such as bovine serum albumin is discussed on the basis of the RGS theory by examining a set of parameters: the degree of polarization, ellipticity, azimuth, and handedness of the ellipse of the polarized component of the scattered light.

Theory

General Consideration. Let us consider the light scattered by a small, optically anisotropic and spheroidal particle whose symmetrical center is situated in the center of the scattering cell. We will consider the effect of the anisotropy on the optical polarizability, that is, the intrinsic (structural) anisotropy. The intrinsic anisotropy occurs when the dispersed phase (the material composing the particle) itself has optical anisotropy.[10] If the dispersed spheroid is optically uniaxial, the excess polarizability, which is the difference between the polarizabilities of the particle and the medium, can be expressed by a spheroid, i.e., $(\alpha_a,\alpha_b,\alpha_b)$, while the optical anisotropy is given by this ratio:

$$p_g = \alpha_a/\alpha_b. \tag{1}$$

In the following discussion, it is reasonable to assume that the direction of the principal polarizability of the spheroid is in agreement with that of the symmetry a-axis of the spheroid.

If the principal refractive indices divided by the refractive index of the solvent n_0 are (m_a,m_b,m_b), the intrinsic (structural) anisotropy p_m is defined by:

$$p_m = (m_a{}^2 - 1)/(m_b{}^2 - 1), \tag{2}$$

and the mean relative refractive index m is defined by reference to the equation of the index ellipsoid:

$$1/(m^2 - 1) = [1/(m_a{}^2 - 1) + 2/(m_b{}^2 - 1)]/3. \tag{3}$$

Scattering Matrix. All possible states of scattered light can easily be analyzed by using the Stokes parameters and the Mueller or scattering matrix, which depends only on the characteristics of the scattering medium.

If the particle is sufficiently small compared to the wavelength of light, the scattering matrix $\boldsymbol{M}$ for a randomly oriented spheroid is given by the RGS theory with the help of the matrix element:[11]

$$\boldsymbol{M} = \begin{vmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{22} & 0 & 0 \\ 0 & 0 & S_{33} & 0 \\ 0 & 0 & 0 & S_{44} \end{vmatrix}, \tag{4}$$

where the matrix elements, S_{11}, S_{12}, S_{22}, S_{33}, and S_{44}, are given for the optically anisotropic spheroid

$$\begin{aligned} S_{11} &= F_1(1+\cos^2\theta)+F_2, \\ S_{12} &= F_1(\cos^2\theta-1), \\ S_{22} &= F_1(\cos^2\theta+1), \\ S_{33} &= 2F_1\cos\theta, \\ S_{44} &= 2(F_1-F_2)\cos\theta, \end{aligned} \tag{5}$$

where:

$$\begin{aligned} F_1 &= F_0(p_g^2+3p_g+7/2), \\ F_2 &= F_0(p_g-1)^2, \\ F_0 &= (x^6/135p^4)\{(m^2-1)(1+2p_m)/ \\ &\quad [3p_m+(m^2-1)(1+2p_m)L_b]\}^2. \end{aligned} \tag{6}$$

The x is the size parameter defined by:

$$x = 2\pi a/\lambda, \tag{7}$$

where λ is the wavelength of light in the medium. The anisometry, i.e., the form anisotropy, is expressed by the axial ratio of the spheroid:

$$p = a/b, \tag{8}$$

while the shape parameter L_b in the b-direction is only a function of axial ratio p, as has been shown in a previous paper.[10]

A particle of isotropic material has the same relative refractive index m in all directions of an electric vector of light, independent of the particle form. Therefore, in the case of the anisometric particle made of the isotropic phase (p_m=1), we obtain:

$$\begin{aligned} F_1 &= (A^2+2AB/3+2B^2/15)/2, \\ F_2 &= 2B^2/15, \\ p_g &= 1+B/A. \end{aligned} \tag{9}$$

These results agree with those obtained in a previous paper.[5] Here, A and B are functions of m, and the axial ratio p as defined by Eq. 15 in Ref. 5.

State of Polarization of the Scattered Light. The scattered light is, in general, partially polarized, and behaves as an incoherent sum of the polarized, I_p, and the unpolarized, I_u, components, which are defined in terms of time averages of the electric-field components of an electromagnetic wave. To give a complete description of a partially elliptically polarized beam of scattered light, we should state the intensities associated with both polarized and unpolarized components, and also give the full specifications of the polarization ellipse.

If we consider a linearly polarized incident light whose electric vector makes an angle ψ with the scattering plane, we can calculate each parameter of partially polarized scattered light with the help of the Stokes parameters and the scattering matrix as follows:

$$\begin{aligned} I_p &= I_p^\circ(1-\cos^2\psi\sin^2\theta), \\ I &= I_p^\circ(1-\cos^2\psi\sin^2\theta)+I_u, \\ I_p^\circ &= 2F_1,\ I_u = 2F_2, \\ \eta &= 0. \end{aligned} \tag{10}$$

The I_u term is contributed only by the F_2 term, showing the optical anisotropy analogously to the cases of an optically isotropic spheroid and an optically anisotropic sphere.

The ellipticity η of the polarized component of scattered light is always equal to 0, which means that the polarized component for an anisotropic spheroid is linearly polarized in the case of linearly polarized incident light.

The azimuth, ζ, of the linearly polarized component of the scattered light is given by:

$$\tan\zeta = \tan\psi/\cos\theta, \tag{11}$$

and is only a function of ψ and θ, it is independent of m, p, x, and p_m in the case of an anisotropic spheroid. The ζ has the same sign as ψ for the forward scattering ($0<\theta<90°$), while it has the opposite sign for the backward scatterig($90°<\theta<180°$).

The degree of polarization, P, defined as the ratio of the intensity of the polarized portion to the intensity, is given by Eq. 10:

$$\begin{aligned} P_\psi(\theta) &= (1-\sin^2\theta\cos^2\psi)/[(1-\sin^2\theta\cos^2\psi)+(F_2/F_1)], \\ F_2/F_1 &= (p_g-1)^2/(p_g^2+3p_g+7/2), \end{aligned} \tag{12}$$

and depends on p, p_m, m, θ, and ψ. In the case of isotropic spherical particles (p_m=1), the $P_\psi(\theta)$ is always equal to 1 over the entire range of θ. For an anisotropic sphere ($p_m \neq 1$, p=1) and an optically isotropic (p_m=1, $p \neq 1$) or anisotropic ($p_m \neq 1$, $p \neq 1$) spheroid, the $P_\psi(\theta)$ is smaller than 1.0, but it is independent of x, as far as RGS theory holds.

Numerical Results and Discussion

Variation of the Intensity of the Scattered Light. The numerical calculations were made with an ACOS 850/20 Computer at the Computer Center of the Ministry of Agriculture and Forestry. Figure 1 shows the variation in the intensities of the scattered light for the unpolarized component I_u and the maximum of the polarized component I_p° as a function of the intrinsic anisotropy p_m for m=1.20. The I_u depends strongly on the p_m value. Here, the quantity I is called the "intensity" of the scattered light, but it is a dimensionless quantity which is equal to the Rayleigh ratio

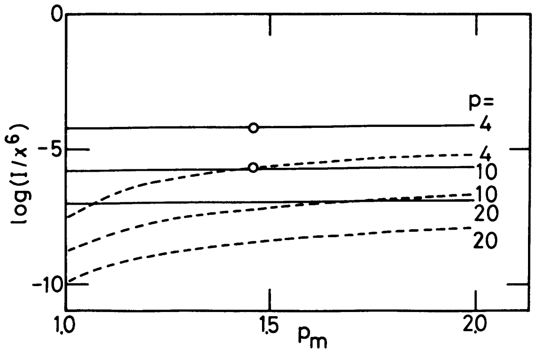

Fig. 1. Variation of $\log(I_u/x^6)$ (dotted lines) and $\log(I_p{}^o/x^6)$ (solid lines) with the intrinsic anisotropy $p_m>1$ for $m=1.20$. Open circles show bovine serum albumin molecule.

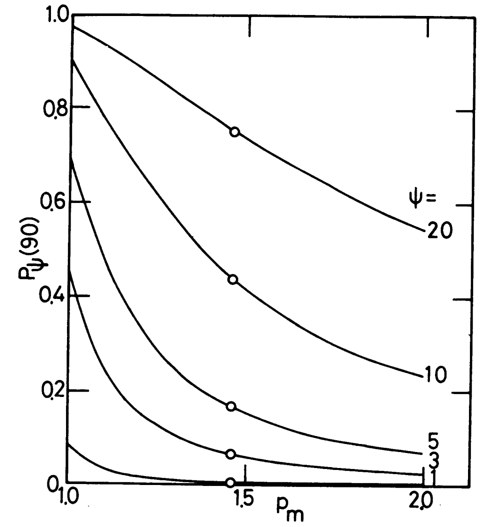

Fig. 2. Variation of the degree of polarization at $\theta=90°$, $P_\psi(90)$, with the intrinsic anisotropy $p_m>1$ and $m=1.20$ and $p=4$ for various values of ψ(degree). Open circles show bovine serum albumin molecule.

per particle multiplied by k^2 (where $k=2\pi/\lambda$) and is usually expressed by i.

Bovine serum albumin in a native state is a globular protein, and its overall molecular shape may be represented as a prolate spheroid whose major semiaxis and minor semiaxis are 7.1 and 1.7 nm respectively.[4] The intrinsic anisotropy parameter of bovine serum albumin is calculated to be $p_m=1.46$ with the refractive index increment and the scattering ratio at a scattering angle of 90°.[3] For such a spheroidal particle, it is reasonable to assume that the direction of the principal polarizability of the spheroid is in agreement with that of the symmetry a-axis of the spheroid; therefore, it is satisfactory to think of the case of $m_a>m_b$, i.e., the values of $p_m>1$, and also to think about the values of $p_m<2.0$.

Variation in the Degree of Polarization. The degree of polarization at $\theta=90°$, as given by Eq. 12, is:

$$P_\psi(90) = \sin^2\psi/(\sin^2\psi + F_2/F_1). \tag{13}$$

Figure 2 shows the variation in $P_\psi(90)$ with the intrinsic anisotropy p_m and ψ, especially in cases in which the ψ is from 1° to 20°.

Figure 3 shows the variation in $P_\psi(90)$ with $\pm\psi$. The $P_\psi(90)$ increases monotonously from 0 to almost 1 with the increase in $|\psi|$, its value becomes smaller, however, as the p_m deviates from the isotropic materials ($p_m=1$).

Determination of Parameter Values. The scattering ratio is defined by the ratio of the intensity scattered at $\theta=90°$ for the incident light vibrating perpendicular to and parallel to the plane of observation. The scattering ratio is of the same numerical value as the depolarization ratio, which is defined by the ratio of the intensity of the parallel component to the perpendicular component of the scattered light for an unpolarized incident beam, when the orientation of the particle is assumed to be completely random. However, the latter has an experimental disadvantage, for perfectly unpolarized incident light is rather difficult to obtain.

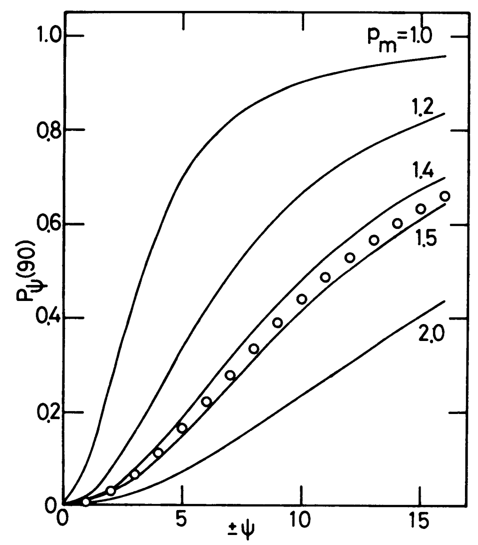

Fig. 3. Variation of the degree of polarization at $\theta=90°$, $P_\psi(90)$, with ψ(degree) and $m=1.20$ and $p=4$ for various values of $p_m>1$. Open circles show bovine serum albumin molecule.

The degree of polarization can also be measured by rotating the polarizer, similar to the case of the scattering ratio. Although only the two special cases of parallel to ($\psi=0$) and perpendicular to ($\psi=90°$) the scatterring plane are discussed in the case of the scattering ratio, the degree of polarization can be mainly used for small ψ values, as is shown in Figs. 2 and 3. The degree of polarization depends strongly on the intrinsic anisotropy p_m, and it is independent of x. If we measure the $P_\psi(90)$ value, the intrinsic (structual) anisotropy can be determined directly from the curvefitting method to the theoretical values.

Knowledge about p_m and m gives information regarding the refractive index of both the a- and b-axes of the spheroid if the refractive index of the solvent is known.

In conjunction with the knowledge of the intrinsic anisotropy p_m, the value of x is obtained from the intensities, I, I_p, and I_u, and the knowledge of x immediately gives information on the molecular weight if the partial specific volume is known.

The theory presented in this paper can be efficiently applied to relatively small p_m values, as is shown in Fig. 3.

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