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WHAT IS THE SYMMETRY OF CASTOR OIL BETWEEN METAL ELECTRODES?

Presented experimental data show that castor oil between metal flat electrodes can not be satisfactorily described as an isotropic liquid of ∞∞ symmetry, even in the absence of an electric field between the electrodes. Correct description of optical properties requires the assumption of ∞2 symmetry and consideration of circular birefringence, linear birefringence and dichroism occurring at the same time. Disappearance of linear birefringence and dichroism in castor oil has been observed several days after filling cuvette witch metal electrodes, which suggests the usefulness of such measurements to study the aging processes. The results presented are also important for correct interpretation of future measurements of electro-optic and electrogyration effects in liquids.

Keywords: castor oil, optical activity, linear birefringence, dichroizm.

1. INTRODUCTION

Castor oil is a viscous liquid extracted from castor beans through cold-pressing. Castor oil is a mixture composed mainly of triglycerides of fatty acids, in which the content of components varies depending on the origin and literature. Among triglycerides ricinoleic acid chains (Fig. 1) have a share of 80%-95%, oleic acid 4%-9%, linoleic acid 3%-5%, stearic acid 1%-3%, palmitic acid 1%-2%, and in small amounts (<1%) vaccenic acid, alpha-linolenic acid, arachidic acid, and eicosenoic acid. The content of free fatty acids in castor oil is 0.75%-3.0%, water content 0.25%-0.5%, and other impurities from 0.01% to 0.2%.

Our preliminary measurements of quadratic electro-optic effect in castor oil have shown that such measurements can be useful to study its aging [1]. The correct mathematical description of optical and electro-optical properties of a given liquid requires a knowledge of the relevant Curie group describing the internal symmetry of the liquid. As the castor oil is known for its optical activity, there are three possible groups: $\infty\infty$, $\infty 2$ or ∞. Among these groups, only $\infty\infty$ characterize an optically active and isotropic liquid. The aim of this paper is to present experimental results and theoretical analysis, which indicate that the correct description of castor oil between metal electrodes requires the assumption of $\infty 2$ symmetry together with significant dichroism. As the contact of the castor oil with stainless steel electrodes turned out to induce the optical axis perpendicular to the planes of the electrodes, we focused in this study on the optical properties in the absence of the electric field. However, the results are also important for the interpretation of the measurements with an applied external electric field.

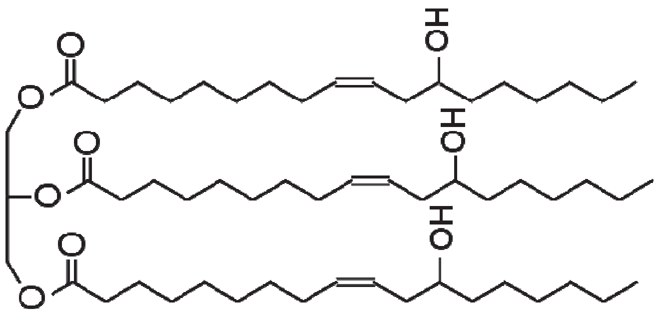

Fig. 1. Structure of ricinoleic acid triglyceride.

2. MATHEMATICAL MODEL

Let us consider a system composed of an optically active liquid in a cuvette in the form of a right parallelepiped placed between linear polarizer and analyzer. We assume that two plane-parallel metal plates parallel to the light beam passing between the plates are immersed in the liquid and affecting the orientation of the particles of the liquid. The intensity of the light I emerging from the system can be derived using the Jones calculus. A fully polarized light wave propagating in the $+z$ direction is represented by the two-element Jones vector $\boldsymbol{\mathcal{E}} = [\mathcal{E}_x, \mathcal{E}_y]$ built from x and y components of the electric field of this light wave. The state of the light emerging from the system is given by the formula $\boldsymbol{\mathcal{E}} = \mathbf{M_2}\,\mathbf{M_1}\,\boldsymbol{\mathcal{E}}_0$, where $\boldsymbol{\mathcal{E}}_0$ is the Jones vector corresponding to the light beam behind the linear polarizer, $\mathbf{M_1}$ is the Jones M-matrix representing a transformation of the light in the sample of the liquid, and $\mathbf{M_2}$ represents the analyzer. The intensity of the light described by the $\boldsymbol{\mathcal{E}}$ vector is given by $I = |\mathcal{E}_x|^2 + |\mathcal{E}_y|^2$.

A general form of the Jones M-matrix, valid for dichroic homogeneous elliptic birefringent media, has been derived by Ścierski & Ratajczyk [2]

$$\mathbf{M} = \begin{bmatrix} T_\mathrm{f}\cos^2\beta + T_\mathrm{s}\sin^2\beta\,\mathrm{e}^{-i\Gamma}, & \sin\beta\cos\beta\left(T_\mathrm{f} - T_\mathrm{s}\mathrm{e}^{-i\Gamma}\right)\mathrm{e}^{-i\delta} \\ \sin\beta\cos\beta\left(T_\mathrm{f} - T_\mathrm{s}\mathrm{e}^{-i\Gamma}\right)\mathrm{e}^{i\delta}, & T_\mathrm{f}\sin^2\beta + T_\mathrm{s}\cos^2\beta\,\mathrm{e}^{-i\Gamma} \end{bmatrix}, \tag{1}$$

where T_f and T_s are the amplitude transmission coefficients for the fast and slow waves, respectively, β is the azimuth $(0 \le \beta \le \pi/2)$ of the diagonal of the rectangle in which the polarization ellipse of the fast wave is inscribed, δ is the phase difference occurring between the y and x components of the electric vector for both the fast and slow waves, and Γ is the phase difference between the slow and fast waves

$$\Gamma = \frac{2\pi l}{\lambda}(n_\mathrm{s} - n_\mathrm{f})\,. \tag{2}$$

The λ in Eq. (2) is the wavelength of the light, l is the length of the cuvette with the liquid, and n_f and n_s are the refractive indices of the fast and slow waves, respectively.

In calculations performed for media manifesting both circular and linear birefringence the Jones matrix in the form given by Eq. (1) is difficult to direct use. The optical properties of such media are usually described by complex relative permittivity tensor $[K_{ij}]$ at the optical frequency or relative impermeability tensor $[B_{ij}]$ defined as $[K_{ij}]^{-1}$. Direct relationships between the terms appearing in the matrix (1) and the B_{ij} components have been recently found using the eigenvalue approach [3]. These formulas take a particularly simple form in such coordinate systems $X'Y'Z'$, in which the light propagates along the $+Z'$ axis, while the choice of the orientation of the X' axis (which defines the reference zero azimuth in the optical system) is arbitrary

$$\sin\beta = \frac{m_{Y'}}{\sqrt{m_{X'}^2 + m_{Y'}^2}} = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{B'_{22} - B'_{11}}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}}\,, \tag{3}$$

$$\cos\beta = \frac{m_{X'}}{\sqrt{m_{X'}^2 + m_{Y'}^2}} = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{B'_{22} - B'_{11}}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}}\,, \tag{4}$$

$$\sin\beta\cos\beta\,\mathrm{e}^{i\delta} = \frac{B'^{*}_{12}}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}\,, \tag{5}$$

$$\sin\beta\cos\beta\,\mathrm{e}^{-i\delta} = \frac{B'_{12}}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}\,, \tag{6}$$

and the refractive indices appearing in formula (2) are given by

$$n_{\mathrm{f}} = \sqrt{\frac{2}{B'_{11} + B'_{22} + \sqrt{\left(B'_{11} - B'_{22}\right)^2 + 4B'_{12}B'^{*}_{12}}}}\,, \tag{7}$$

$$n_{\mathrm{s}} = \sqrt{\frac{2}{B'_{11} + B'_{22} - \sqrt{\left(B'_{11} - B'_{22}\right)^2 + 4B'_{12}B'^{*}_{12}}}}\,. \tag{8}$$

Equations (3)-(8) were derived under the assumption that the real part of the impermeability tensor is symmetric and the imaginary one is antisymmetric $B'_{ij} = B'^{*}_{ji}$. This assumption is not exactly fulfilled in absorbing mediums (T_{f}, $T_{\mathrm{s}} < 1$). However, the asymmetry is very small [4] and is omitted in further calculations.

The above formulae allow us to find the intensity of the light passing through the system consisting of the sample of liquid between the linear polarizer and analyzer. We assume that the polarizer and analyzer are ideal elements, the polarizer azimuth is 0, and the azimuth of the analyzer is any fixed value α_{a} relative to the axis X'. In the case of the liquid we allow any transmissions T_{f} and T_{s}, any elliptical polarization of eigenwaves, and any orientation of the optical axis (if the axis exists). The intensity of the emerging light I relative to the intensity I_{p} behind the polarizer is given by the formula

$$\begin{aligned}
\frac{I}{I_{\mathrm{p}}} = {} & \frac{1}{4}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) + \cos^2(\alpha_{\mathrm{a}})\left(T_{\mathrm{s}}^2 - T_{\mathrm{f}}^2\right)\frac{B'_{22} - B'_{11}}{2\sqrt{(B'_{22} - B'_{11})^2 + 4B'_{12}B'^{*}_{12}}} + \\
& + \left(\cos^2\alpha_{\mathrm{a}} - \sin^2\alpha_{\mathrm{a}}\right)\left[\frac{1}{4}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) - \frac{B'_{12}B'^{*}_{12}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2 - 2T_{\mathrm{f}}T_{\mathrm{s}}\cos\Gamma\right)}{(B'_{22} - B'_{11})^2 + 4B'_{12}B'^{*}_{12}}\right] + \\
& + \sin\alpha_{\mathrm{a}}\cos\alpha_{\mathrm{a}}\left[\frac{\left(T_{\mathrm{f}}^2 - T_{\mathrm{s}}^2\right)\mathrm{Re}[B'_{12}]}{\sqrt{(B'_{22} - B'_{11})^2 + 4B'_{12}B'^{*}_{12}}} + \right. \\
& \qquad + \frac{\mathrm{Re}[B'_{12}](B'_{11} - B'_{22})}{(B'_{22} - B'_{11})^2 + 4B'_{12}B'^{*}_{12}}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2 - 2T_{\mathrm{f}}T_{\mathrm{s}}\cos\Gamma\right) + \\
& \qquad \left. + 2T_{\mathrm{f}}T_{\mathrm{s}}\frac{\mathrm{Im}[B'_{12}]}{\sqrt{(B'_{22} - B'_{11})^2 + 4B'_{12}B'^{*}_{12}}}\sin\Gamma\right].
\end{aligned} \tag{9}$$

The assumption that the azimuth of polarizer is equal to 0 simplifies the formula without losing generality. Any orientation of the polarizer relative to the other elements can be taken into account by an appropriate choice of the experimental coordinate system $X'Y'Z'$.

The real part of permittivity and impermeability tensors Re[K_{ij}] and Re[B_{ij}] does not depend on the direction of the light propagation. The imaginary part of permittivity tensor can be always written as a second-rank antisymmetric tensor composed of the components of the vector **G** = [G_1, G_2, G_3] [5]

$$\mathrm{Im}[K]=[G]=\begin{bmatrix} 0 & -G_3 & G_2 \\ G_3 & 0 & -G_1 \\ -G_2 & G_1 & 0 \end{bmatrix}. \tag{10}$$

The gyration vector **G** for the given direction of the light beam **s** can be found as

$$\mathbf{G} = [g]\mathbf{s}, \tag{11}$$

where [g] is the second-rank axial gyration tensor with real components, which are independent of **s**.

Using the definition of the impermeability tensor $[B]=[K]^{-1}$ it can be shown that the imaginary antisymmetric part of the tensor [K] determines analogous part of the tensor [B] according to the formula [6]

$$\mathrm{Im}[B] = -(\mathrm{Re}[B])[G](\mathrm{Re}[B]). \tag{12}$$

We now consider the application of the formulae (9)-(12) to any optically active liquid in the absence of any applied electric or magnetic field, which can belong to one of three Curie groups: ∞∞, ∞2 or ∞.

2.1. Liquid of the ∞∞ symmetry

In the case of medium with the symmetry ∞∞ in the absence of any applied electric or magnetic field

$$\mathrm{Re}[B]=\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & 0 \\ 0 & 0 & n_{01}^{-2} \end{bmatrix}, \qquad [g]=\begin{bmatrix} g_{11}^{(0)} & 0 & 0 \\ 0 & g_{11}^{(0)} & 0 \\ 0 & 0 & g_{11}^{(0)} \end{bmatrix}. \tag{13}$$

Tensors (13) describe an isotropic medium, i.e. any rotation of the coordinate system should not affect the form of these tensors. However, this result does not agree with our observations made for the castor oil between metal electrodes. Our measurements show that the orientation of the polarizer relative to the cuvette with the oil and electrodes clearly affects the results (see Chapter 3).

2.2. Liquid of the ∞2 or ∞ symmetry

In the absence of any applied external field the tensors Re[B] and [g] have the same form for liquids of the ∞2 and ∞ symmetries. These tensors have the following components in XYZ coordinate system, in which $+Z$ is the optical axis

$$\mathrm{Re}[B]=\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & 0 \\ 0 & 0 & n_{03}^{-2} \end{bmatrix}, \quad [g]=\begin{bmatrix} g_{11}^{(0)} & 0 & 0 \\ 0 & g_{11}^{(0)} & 0 \\ 0 & 0 & g_{33}^{(0)} \end{bmatrix}. \qquad (14)$$

The results of our measurements indicate that the optical axis in castor oil is oriented perpendicularly to the plane of the electrodes immersed in the oil, thus the $+X$ axis may be selected in the direction of the light beam propagating along the electrodes. The tensors (14) and $\mathbf{s} = [1, 0, 0]$ substituted into Eqs. (10)-(12) leads to the following total complex impermeability tensor

$$[B]=\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & i\,n_{01}^{-2}n_{03}^{-2}g_{11}^{(0)} \\ 0 & -i\,n_{01}^{-2}n_{03}^{-2}g_{11}^{(0)} & n_{03}^{-2} \end{bmatrix}. \qquad (15)$$

The components B_{ij} given by Eq. (15) require transformation from the XYZ to the $X'Y'Z'$ coordinates before substitution into formula (9). We will build this transformation as a composition of two simpler transformations:

1. The transformation of XYZ to an intermediate coordinates $X_1Y_1Z_1$, in which the light direction $\mathbf{s}$ coincides with the axis $+Z_1 = +X$, the optical axis is $+X_1 = +Z$, and $+Y_1 = -Y$.
2. The polarizer orientation angle $+\theta$ relative to the optical axis in the oil will be taken into account by performing a transformation of the B_{ij}^{1} components given in $X_1Y_1Z_1$ coordinates to the experimental coordinates $X'Y'Z'$ with the axes X' and Y' rotated around $+Z_1 = Z'$ through the angle $+\theta$.

The total transformation matrix from the XYZ to the $X'Y'Z'$ system has therefore the form

$$\mathbf{a}=\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{bmatrix}. \qquad (16)$$

After the transformation $[B'] = \mathbf{a}[B]\mathbf{a}^{\mathrm{T}}$ one obtains the following components

$$\begin{aligned} B'_{11} &= n_{03}^{-2}\cos^2\theta + n_{01}^{-2}\sin^2\theta, \\ B'_{22} &= n_{03}^{-2}\sin^2\theta + n_{01}^{-2}\cos^2\theta, \\ B'_{12} &= (n_{01}^{-2} - n_{03}^{-2})\sin\theta\cos\theta + i\, n_{01}^{-2} n_{03}^{-2} g_{11}^{(0)}. \end{aligned} \tag{17}$$

Equation (9) with substituted (17) in it takes the following form

$$\frac{I}{I_{\mathrm{p}}} = \frac{1}{4}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) + \frac{1}{2}A\cos^2(\alpha_{\mathrm{a}}) + \frac{1}{4}C\left(\cos^2\alpha_{\mathrm{a}} - \sin^2\alpha_{\mathrm{a}}\right) + D\sin\alpha_{\mathrm{a}}\cos\alpha_{\mathrm{a}}, \tag{18}$$

where

$$A = \left(T_{\mathrm{s}}^2 - T_{\mathrm{f}}^2\right)\frac{\left(n_{03}^{-2} - n_{01}^{-2}\right)\cos(2\theta)}{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}}, \tag{19}$$

$$\begin{aligned} C &= \left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) + \\ &- \frac{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2\sin^2(2\theta) + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}\left[\left(T_{\mathrm{f}} - T_{\mathrm{s}}\right)^2 + 2T_{\mathrm{f}}T_{\mathrm{s}}\left(1 - \cos\Gamma\right)\right], \end{aligned} \tag{20}$$

$$\begin{aligned} D &= -\frac{\left(T_{\mathrm{f}}^2 - T_{\mathrm{s}}^2\right)\left(n_{03}^{-2} - n_{01}^{-2}\right)\sin(2\theta)}{2\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}} + \\ &- \frac{1}{4}\frac{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2\sin(4\theta)}{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}\left[\left(T_{\mathrm{f}} - T_{\mathrm{s}}\right)^2 + 2T_{\mathrm{f}}T_{\mathrm{s}}\left(1 - \cos\Gamma\right)\right] + \\ &+ 2T_{\mathrm{f}}T_{\mathrm{s}}\frac{n_{01}^{-2}n_{03}^{-2}g_{11}^{(0)}}{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}}\sin\Gamma. \end{aligned} \tag{21}$$

The refractive indices n_{f} and n_{s}, which are necessary to calculate the phase difference Γ, are given by the exact formulas (7) and (8), respectively. Since the results of our measurements shows that $n_{03}^{-2} + n_{01}^{-2} >>$ $>> \left[\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}\right]^{1/2}$ we can use the approximation

$$n_{\mathrm{f}} \approx \sqrt{\frac{2}{n_{03}^{-2} + n_{01}^{-2}}} - \frac{\sqrt{2}}{2}\frac{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}}{(n_{03}^{-2} + n_{01}^{-2})^{3/2}}, \tag{22}$$

$$n_{\mathrm{s}} \approx \sqrt{\frac{2}{n_{03}^{-2}+n_{01}^{-2}}+\frac{\sqrt{2}}{2}\frac{\sqrt{\left(n_{03}^{-2}-n_{01}^{-2}\right)^2+4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}}{(n_{03}^{-2}+n_{01}^{-2})^{3/2}}}\,. \tag{23}$$

Thus, and from equation (2) one obtains

$$\Gamma \approx \frac{2\sqrt{2}\,\pi l}{\lambda}\,\frac{\sqrt{\left(n_{03}^{-2}-n_{01}^{-2}\right)^2+4n_{01}^{-4}n_{03}^{-4}g_{11}^{(0)2}}}{(n_{03}^{-2}+n_{01}^{-2})^{3/2}}\,. \tag{24}$$

Equation (18) with substituted formulas (19)-(21) and (24) has an involved form for $g_{11}^{(0)}$ and $n_{01}-n_{03}$. However, for the maximum light path-length in our measurements $l = 0.1$ m the Γ value is of the order of several degrees, and we can use the following approximations

$$\sin\Gamma \approx \Gamma, \quad (1-\cos\Gamma) \approx \Gamma^2/2, \tag{25}$$

while a more rough approximation $\cos\Gamma \approx 1$ seems to be insufficient. Moreover, our measurement results show that $|n_{01} - n_{03}| << n_{01} + n_{03}$ and we can use a single average refractive index n_0 to simplify writing expressions

$$n_{01}n_{03} \approx n_0^2 \quad \text{and} \quad n_{03}^{-2}+n_{01}^{-2} \approx 2n_0^{-2}\,. \tag{26}$$

The approximations (25) and (26) will be included in further formulas given in Chapter 3.

Substitution of Eq. (18) into the condition $\partial(I/I_{\mathrm{p}})/\partial\alpha_{\mathrm{a}} = 0$ leads to the conclusion that the intensity of emerging light reaches extremes for the following azimuths of the analyzer

$$\tan(2\alpha_{\mathrm{a}}) = 2D/(A+C)\,. \tag{27}$$

In general, the light coming from the oil sample can be polarized elliptically, so we can not use the concept of the angle of turning of the polarization plane in the oil. Therefore, we will use a more general angle ϕ of turning of the major axis in the polarization ellipse. As the polarizer azimuth is assumed to be 0 in the $X'Y'Z'$ coordinates, the angle ϕ is associated with experimental value of α_a found for the minimum of I by the formula $\phi = \alpha_a \pm 90°$, and we get that

$$\tan(2\phi) = \tan(2\alpha_a). \tag{28}$$

Now we consider the dependencies of extreme intensities of emerging light I_{max} and I_{min} on the angle θ. The formula (27) shows that the extremes of I are achieved for the following values of $\sin(2\alpha_a)$ and $\cos(2\alpha_a)$

$$\sin(2\alpha_{\mathrm{a}}) = \pm 2D\Big/\sqrt{(A+C)^2+4D^2}\,, \tag{29}$$

$$\cos(2\alpha_{\mathrm{a}}) = \pm(A+C)\Big/\sqrt{(A+C)^2+4D^2}\,. \tag{30}$$

After substitution of Eqs. (29) and (30) into (18) one obtains

$$\frac{I_{\min,\max}}{I_{\mathrm{p}}} = \frac{1}{4}\left(T_{\mathrm{f}}^2+T_{\mathrm{s}}^2\right)+\frac{1}{4}A\pm\frac{1}{4}\sqrt{(A+C)^2+4D^2}\,, \tag{31}$$

where the sign „+” corresponds to the maximum $I_{\max}$, and „–” corresponds to the minimum $I_{\min}$.

The formulas derived in this section allow estimation of the values of $g_{11}^{(0)}$, $n_{01}-n_{03}$, and $|T_{\mathrm{f}}-T_{\mathrm{s}}|/(T_{\mathrm{f}}+T_{\mathrm{s}})$ on the basis of experimental dependencies of ϕ and $I_{\min}/I_{\max}$ on the angle θ between the polarizer azimuth and the optical axis in castor oil.

3. MEASUREMENT RESULTS AND DISCUSSION

Castor oil produced by PROLAB and kept in the original airtight bottle was poured into open glass cuvette with a length $l = 10$ cm, and two plane-parallel stainless steel plates with a length similar to the length of the cuvette and a distance $d = 8$ mm were immersed in the oil. The cuvette was placed between two linear polarizers and illuminated with He-Ne laser Melles Griot 05–LHP–171 at a wavelength $\lambda = 632.8$ nm, and the light beam was directed parallel between the metal plates. The intensity of the light I emerging from the system was measured using a photodiode Thor-Labs PDA100A–EC and a digital multimeter Keithley 2000 DMM in DC voltmeter mode. Our experiments were performed at room temperature with no voltage applied to the metal electrodes, so contact of the oil with the metal plates was the only reason of orientational arrangement of the oil molecules. The average refractive index of castor oil was $n_0 = 1.48$.

In the particular case where $T_{\mathrm{s}} = T_{\mathrm{f}}$ formula (27) (with substituted equations (19)-(21), (24) and approximations (25) and (26)) simplifies to the form

$$\tan(2\phi) = \frac{-\dfrac{\pi^2 l^2}{4\lambda^2}n_0^6\left(n_{03}^{-2}-n_{01}^{-2}\right)^2\sin(4\theta)+2\dfrac{\pi l}{\lambda}n_0^{-1}g_{11}^{(0)}}{1-\dfrac{\pi^2 l^2 n_0^6}{2\lambda^2}\left[\left(n_{03}^{-2}-n_{01}^{-2}\right)^2\sin^2(2\theta)+4n_0^{-8}g_{11}^{(0)2}\right]}\,. \tag{32}$$

However, our experimental dependence of the angle ϕ on θ (Fig. 2) shows first of all the changes proportion to $-\sin(2\theta)$, that can not be described by the formula (32). The experimental data can be fitted by equation (27) only when we admit simultaneously $T_s \neq T_f$, $n_{01} \neq n_{03}$ and $g_{11}^{(0)} \neq 0$. In this general case, the exact series expansion of the theoretical dependence of tan(2ϕ) on θ requires consideration of all components in the Fourier series, but a good approximation can be achieved with the following sum

$$\tan(2\phi) = a_0 + a_2\cos(2\theta) + b_2\sin(2\theta) + b_4\sin(4\theta)\,. \qquad (33)$$

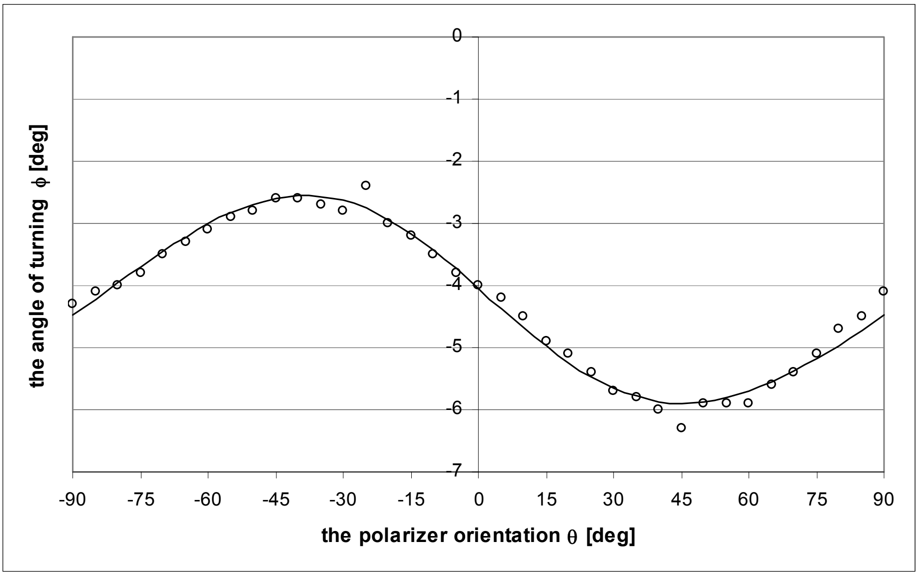

Fig. 2. Experimental dependence of the angle ϕ of turning the major axis in the light polarization ellipse after passing through castor oil sample as a function of the polarizer orientation θ. The interpolation is plotted according to Eq. (33).

The experimental results shown in Fig. 2 correspond to the following values of the coefficients $a_0 = -0.14985$; $a_2 = 0.00737$; $b_2 = -0.05882$ and $b_4 = -0.00316$. As the values obtained for a_2 and b_4 are comparable to the measurement error 2Δϕ, they are not suitable for further calculations. The coefficient a_0 is related to both the $g_{11}^{(0)}$ and the transmission coefficients T_f and T_s. Assuming a small difference in the transmissions $|T_f - T_s| << T_f + T_s$ we can estimate

$$g_{11}^{(0)} \approx \frac{2T_f T_s}{T_f^2 + T_s^2}\, g_{11}^{(0)} = \frac{\lambda n_0}{2\pi l} a_0 \approx -2.2\cdot 10^{-7}\,. \qquad (34)$$

The known values of the coefficients a_0 and b_2 do not allow independent evaluation of the linear birefringence nor dichroism, but lead to the conclusion that both of these phenomena significantly affect the observed dependence ϕ on θ

$$\frac{T_{\mathrm{f}}^2 - T_{\mathrm{s}}^2}{T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2} \frac{\left(n_{03}^{-2} - n_{01}^{-2}\right)}{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_{01}^{-4} n_{03}^{-4} g_{11}^{(0)2}}} \approx -b_2 = 0.05882\,. \tag{35}$$

In our subsequent measurements the ratio of the light intensities $I_{\min}/I_{\max}$ versus the angle θ has been investigated. The theoretical dependencies $I_{\min}$ and $I_{\max}$ on θ given by the formula (31) (with substituted equations (19)-(21) and (24)) are rather complicated functions in the general case, but for not too long light path-length l we can use the approximations (25) and (26) as well as we can assume a small difference in the transmission coefficients $|T_{\mathrm{f}} - T_{\mathrm{s}}| << T_{\mathrm{f}} + T_{\mathrm{s}}$. In this situation, the influence of all terms depend on θ, Γ and $T_{\mathrm{f}} - T_{\mathrm{s}}$ on the $I_{\max}$ value turns out to be insignificant and can write

$$\frac{I_{\max}}{I_{\mathrm{p}}} \approx \frac{1}{2}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right). \tag{36}$$

Calculations of $I_{\min}$ using the formula (31) is more complicated due to the difference of two terms, which have very similar values, but we can at least use the approximation

$$\frac{I_{\min}}{I_{\mathrm{p}}} \approx \frac{1}{4}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) - \frac{C}{4} - \frac{D^2}{2\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right)}. \tag{37}$$

Furthermore, the results presented above concerning the tan(2ϕ) on θ dependence show, that the only significant components in Eq. (21), which define the symbol D, are those independent of θ and proportional to sin(2θ). After expanding D^2 without the terms containing sin(4θ), one obtains the formula

$$\begin{aligned}
\frac{I_{\min}}{I_{\max}} \approx {} & \frac{\left(T_{\mathrm{f}} - T_{\mathrm{s}}\right)^4}{8\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right)^2} \frac{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 [1 - \cos(4\theta)]}{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_0^{-8} g_{11}^{(0)2}} + \\
& + \frac{T_{\mathrm{f}} T_{\mathrm{s}}}{4\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right)} \frac{\pi^2 l^2}{\lambda^2} n_0^6 \left(n_{03}^{-2} - n_{01}^{-2}\right)^2 [1 - \cos(4\theta)] + \\
& + 2\frac{\left(T_{\mathrm{f}} - T_{\mathrm{s}}\right)^2}{T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2} g_{11}^{(0)2} \left[\frac{n_0^{-8}}{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_0^{-8} g_{11}^{(0)2}} + \frac{T_{\mathrm{f}} T_{\mathrm{s}}}{T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2} \frac{\pi^2 l^2}{\lambda^2 n_0^2} \right] + \\
& + \frac{2 T_{\mathrm{f}} T_{\mathrm{s}}}{\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right)^2} \frac{\pi l}{\lambda n_0} \frac{\left(T_{\mathrm{f}}^2 - T_{\mathrm{s}}^2\right)\left(n_{03}^{-2} - n_{01}^{-2}\right) g_{11}^{(0)} \sin(2\theta)}{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4n_0^{-8} g_{11}^{(0)2}}}.
\end{aligned} \tag{38}$$

Thus, the experimental dependence of $I_{\min}/I_{\max}$ on θ can be approximated by summing the selected terms from the Fourier series

$$I_{\min}/I_{\max} \approx a_0 + b_2 \sin(2\theta) + a_4 \cos(4\theta)\,. \tag{39}$$

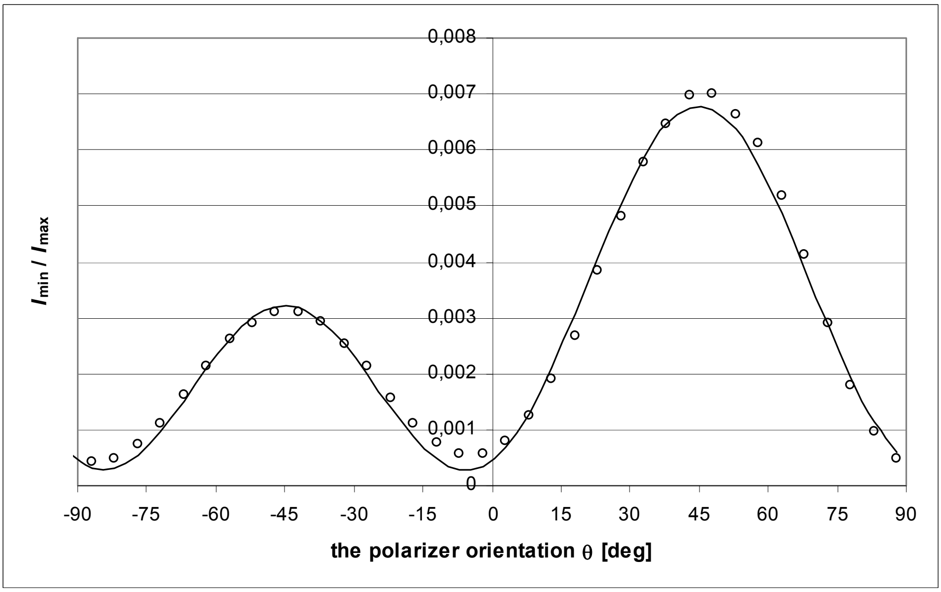

Fig. 3. Experimental dependence of the ratio of the light intensities $I_{\min}/I_{\max}$ on the polarizer orientation θ. The interpolation is plotted according to Eq. (39).

The measurement results presented in Fig. 3 correspond to the following values of the coefficients $a_0 = 0.00272$; $b_2 = 0.00178$ and $a_4 = -0.00227$. Comparison of Eqs. (38) and (39) shows the relationships of a_4 and b_2 with the both $n_{03}^{-2} - n_{01}^{-2}$ and $T_\mathrm{f} - T_\mathrm{s}$ unknowns, and therefore we can eliminate the term $T_\mathrm{f} - T_\mathrm{s}$ and build a quadratic equation with unknown $\left(n_{03}^{-2} - n_{01}^{-2}\right)^2$

$$\begin{aligned}
&\frac{T_\mathrm{f} T_\mathrm{s}}{4\left(T_\mathrm{f}^2 + T_\mathrm{s}^2\right)} \frac{\pi^2 l^2}{\lambda^2} n_0^6 \left(n_{03}^{-2} - n_{01}^{-2}\right)^4 + \\
&+\left[a_4 + b_2^4 \frac{\left(T_\mathrm{f}^2 + T_\mathrm{s}^2\right)^6}{128 T_\mathrm{f}^4 T_\mathrm{s}^4 \left(T_\mathrm{f} + T_\mathrm{s}\right)^4} \frac{\lambda^4 n_0^4}{\pi^4 l^4 g_{11}^{(0)4}}\right]\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + \\
&+ b_2^4 \frac{\left(T_\mathrm{f}^2 + T_\mathrm{s}^2\right)^6}{32 T_\mathrm{f}^4 T_\mathrm{s}^4 \left(T_\mathrm{f} + T_\mathrm{s}\right)^4} \frac{\lambda^4 n_0^4}{\pi^4 l^4 n_0^4 g_{11}^{(0)2}} = 0.
\end{aligned} \tag{40}$$

In the general case, Eq. (40) still contains too many unknowns. However, it is possible to find an approximate solution assuming that $T_f \approx T_s$, which leads to reduction of all terms including T_f and T_s

$$\frac{\pi^2 l^2}{8\lambda^2} n_0^6 \left(n_{03}^{-2} - n_{01}^{-2}\right)^4 + \left[a_4 + b_2^4 \frac{\lambda^4 n_0^4}{32\pi^4 l^4 g_{11}^{(0)4}}\right]\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + b_2^4 \frac{\lambda^4 n_0^4}{8\pi^4 l^4 n_0^4 g_{11}^{(0)2}} = 0. \quad (41)$$

Equation (41) has two solutions, one of which leads to a non-physical value of the difference of the transmission coefficients. The second correct solution is $(n_{03}^{-2} - n_{01}^{-2})^2 \approx 7.0 \cdot 10^{-15}$. Hence the linear birefringence calculated for the average value of $n_0 \approx 1.48$ is

$$| n_{01} - n_{03} | = \frac{1}{2} | n_{03}^{-2} - n_{01}^{-2} | n_0^3 \approx 1.4 \cdot 10^{-7}. \quad (42)$$

Using again the assumption $|T_f - T_s| << T_f + T_s$ the dichroism can be estimated as

$$\frac{|T_f - T_s|}{\overline{T}} \approx |b_2| \frac{\lambda n_0}{\pi l} \frac{\sqrt{\left(n_{03}^{-2} - n_{01}^{-2}\right)^2 + 4 n_0^{-8} g_{11}^{(0)2}}}{\left|\left(n_{03}^{-2} - n_{01}^{-2}\right) g_{11}^{(0)}\right|} \approx 0.036. \quad (43)$$

where $\overline{T}$ is the average transmission coefficient $\overline{T} = (T_f + T_s)/2$.

The results of measurements of the turning angle ϕ and the ratio of the light intensities I_{min}/I_{max} as a functions of the angle θ showed good stability during the period of a few hours, but on subsequent days the fluctuations were observed without clear tendency towards an increase or decrease. The estimated values of $|n_{01} - n_{03}|$ and $| T_f - T_s | / \overline{T}$ should therefore be considered as known with the accuracy to the order of magnitude. After a period of about two weeks spontaneous disappearance of the linear birefringence and the dichroism was observed, while the circular birefringence described by the $g_{11}^{(0)}$ coefficient was stable throughout the observation period.

The results presented in this section show that castor oil placed between metal electrodes initially has the ∞2 or ∞ symmetry, while the disappearance of the linear birefringence and dichroism indicates changes in symmetry towards the ∞∞ Curie group. Since the measurements without the use of any external field are not capable of distinguishing between the ∞2 and ∞ symmetries, we have identified the ∞2 symmetry by examining the linear electro-optic and linear electrogyration effects. It can be shown that there exist such configurations of light modulators, in which the response originating from the linear effects is extinguished for the ∞2 group, and it should be clearly observed in the case of the ∞ group.

4. CONCLUSIONS

Our measurements of the optical properties of castor oil between plane-parallel metal plates indicate that the castor oil in such conditions can not be considered as an isotropic liquid, even in the absence of any applied electric and magnetic fields. The correct fitting of experimental data to theoretical dependencies derived employing Jones calculus requires the assumption that the following phenomena must occur simultaneously in the sample of castor oil:

1) circular birefringence described by the coefficient $g_{11}^{(0)} \approx 2.2 \cdot 10^{-7}$,
2) linear birefringence $|n_{01} - n_{03}| \approx 1.6 \cdot 10^{-7}$, wherein the optical axis is perpendicular to the planes of metal plates,
3) dichroism, i.e., different transmission coefficients for the fast and slow waves $|T_{\mathrm{f}} - T_{\mathrm{s}}| / \overline{T} \approx 0.036$.

Phenomenon (1) appears to be stable, while phenomena (2) and (3) were observed for several days and then disappeared. Thus, the internal symmetry of castor oil can be described as initially $\infty 2$ with optical axis perpendicular to metal plates, which then tends to $\infty\infty$. Therefore, measurements of linear birefringence and dichroism seem to open the possibility of studying the aging processes in castor oil.

The results presented are also important for the correct interpretation of measurements of electro-optic and electrogyration effects in castor oil. These effects can also be used to study the aging processes, but the changes observed should be interpreted very carefully. The changes in response of a light modulator due to an applied electric field may be caused by the changes in electro-optic or electrogyration coefficients as well as the changes in the linear birefringence and dichroism.

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JAKA JEST SYMETRIA OLEJU RYCYNOWEGO POMIĘDZY METALOWYMI ELEKTRODAMI?

Streszczenie

Przedstawiono wyniki pomiarów wskazujące, że olej rycynowy umieszczony pomiędzy metalowymi płaskimi elektrodami nie może być zadowalająco opisany jako ciecz izotropowa o symetrii $\infty\infty$, nawet przy braku pola elektrycznego pomiędzy elektrodami. Poprawny opis właściwości optycznych wymaga założenia symetrii $\infty 2$ oraz uwzględnienia jednocześnie dwójłomności kołowej, dwójłomności liniowej i dichroizmu. Zaobserwowano zanikanie dwójłomności liniowej i dichroizmu w oleju rycynowym po kilkunastu dniach od napełnienia kuwety z metalowymi elektrodami, co wskazuje na przydatność pomiarów tych wielkości do badań procesów starzenia. Przedstawione rezultaty mają także znaczenie dla poprawnej interpretacji przyszłych pomiarów efektów elektro-optycznych i elektrożyracji w cieczach.