SCIENTIFIC BULLETIN OF THE LODZ UNIVERSITY OF TECHNOLOGY
No. 1183 Physics, Vol. 34 2013

MAREK IZDEBSKI, RAFAŁ LEDZION
WŁODZIMIERZ KUCHARCZYK

Institute of Physics, Lodz University of Technology
ul. Wólczańska 219, 90-924 Łódź, Poland, e-mail: izdebski@p.lodz.pl

ANALYSIS OF MEASUREMENT OF QUADRATIC ELECTRO-OPTIC EFFECT IN CASTOR OIL

This works presents an extended theoretical analysis of the response of experimental setup to an applied electric field during measurements of electro-optic coefficients in optically active liquids using an optical polarimetric technique. The analysis includes liquids belonging to ∞∞, ∞2 and ∞ Curie symmetry groups and the following phenomena were taken into account: natural optical activity, natural linear birefringence, dichroism, and the effects induced by an applied electric field – linear and quadratic electro-optic effects and linear and quadratic electrogyration. The presented example concerns numerical error analysis for measurement of the quadratic electro-optic effect in castor oil, which exhibits the symmetry ∞2 between a pair of plane-parallel electrodes.

Keywords: castor oil, electro-optic effects, optical activity, dichroism.

1. INTRODUCTION

The recent results have shown that the measurements of the Kerr constant and its temperature dependence are useful in the study of castor oil aging [1]. A simplified analysis of optical response of the measurement system to the applied external electric field presented previously was derived for an isotropic liquid belonging to the ∞∞*m* Curie group symmetry, which excludes the dichroism, natural linear birefringence, natural optical activity, and the optical activity induced by the applied electric field (also called electrogyration effect). The castor oil, however, is known for its natural optical activity 4-6°/dm [2], which means, that the internal symmetry of the oil must be described by one of the three Curie groups allowing for this phenomenon: ∞∞, ∞2 or ∞. Recent studies have also shown that the correct description of the optical properties of the castor oil between a pair of metal plane-parallel plates with a several millimetres space between them requires consideration of the circular birefringence, linear birefringence, and dichroism occurring at the same time, which means that the oil symmetry can be described only by the ∞2 or ∞ groups [3]. The previous study concerned the interaction between the oil and material of plates in the absence of any applied electric or magnetic field, which did not give any possibility to distinguish between the ∞2 and ∞ groups. However, in the case of measurements with an externally applied field the two symmetries lead to substantially different optical responses.

The aim of this work is to provide an extended theoretical analysis of the optical response to an applied electric field, which appears in the experimental setup employed in measurements of electro-optic coefficients using the optical polarimetric method. The analysis includes the dichroism, natural linear birefringence, natural optical activity and the effects induced by an applied electric field, namely the linear and quadratic electro-optic effects and the linear and quadratic electrogyration. The consequences of transitions between the ∞∞, ∞2 and ∞ symmetries in the sample of liquid are also discussed. Moreover, the measurement conditions were identified in which the manifestation of undesirable effects should not significantly disturb the measurements of electro-optic coefficients. Although this work refers to the measurements in the castor oil, the presented extended analysis may be useful to better understanding of measurements with many other optically active liquids.

2. THEORETICAL ANALYSIS

2.1. Impermeability tensor for optically active liquids

Let us consider any dichroic homogeneous nonmagnetic nondepolarizing elliptically birefringent liquid. The electro-optic effects are defined in terms of changes in the real part of the optical frequency impermeability tensor $[B_{ij}]$ caused by an applied electric field **E**

$$\mathrm{Re}[B_{ij}] = \mathrm{Re}[B_{ij}^{(0)}] + r_{ijk}E_k + q_{ijkl}E_kE_l + \ldots, \quad (1)$$

where $\mathrm{Re}[B_{ij}^{(0)}]$ are the field-free components of the tensor related to the natural linear birefringence, r_{ijk} are the components of the linear electro-optic tensor, and q_{ijkl} are the components of the quadratic electro-optic tensors (Table 1). The real part $\mathrm{Re}[B_{ij}]$ is exactly symmetrical only for non-absorbing media, but the asymmetry associated with the absorption is typically negligibly small and will be omitted in this work. As the absorption should be taken into account in this study, we use the transmission coefficients, which are not explicitly related to the $[B_{ij}]$ tensor.

The imaginary antisymmetric part of the $[B_{ij}]$ tensor represents the optical activity, however, traditionally the optical activity is described with the relative electric permittivity tensor $[K_{ij}]$. The imaginary antisymmetric part of the $[K_{ij}]$ tensor can be written as [4]

$$\mathrm{Im}[K_{ij}] = \begin{bmatrix} 0 & -G_3 & G_2 \\ G_3 & 0 & -G_1 \\ -G_2 & G_1 & 0 \end{bmatrix}, \tag{2}$$

where G_1, G_2 and G_3 are the elements of the gyration vector **G** for a given wave propagation vector **s**

$$\mathbf{G} = [g]\mathbf{s}. \tag{3}$$

In Eq. (3) $[g]$ is a second rank gyration axial tensor described by a real 3×3 matrix. The total optical activity of a liquid exhibiting the natural optical activity and the activity induced by a DC or low-frequency electric field can be expressed by the following power series

$$g_{ij} = g_{ij}^{(0)} + \gamma_{ijk} E_k + \beta_{ijkl} E_k E_l + \ldots, \tag{4}$$

where $g_{ij}^{(0)}$ are the components of field-free gyration tensor describing a natural optical activity, γ_{ijk} are the components of the linear electrogyration tensors, and β_{ijkl} are the components of the quadratic electrogyration tensor (Table 2). The imaginary antisymmetric part of $[B]$ may be found using the formula which follows from the definition of the impermeability tensor $[B] = [K]^{-1}$ [5]

$$\mathrm{Im}[B] = -(\mathrm{Re}[B])(\mathrm{Im}[K])(\mathrm{Re}[B])\,. \tag{5}$$

The formulas (1)-(5) allow us to find the total complex Hermitian tensor $[B]$ for a given directions of the light and applied electric field.

A pair of plane-parallel electrodes immersed in castor oil induce a dichroism and linear birefringence, with the optical axis directed perpendicularly to the electrodes [3]. Thus, the formulas (1)-(5) and Tables 1 and 2 are written for such XYZ coordinates, where the Z axis is associated with the applied electric field $\mathbf{E} = [0, 0, E]$, and the X and Y axes can be chosen freely. In calculations of the light transmission through the system of plane-parallel plates we use, however, another coordinate system $X'Y'Z'$, in which the direction of the light beam **s** defines the $+Z'$ axis and the direction of the field $\mathbf{E} \| X'$.

Table 1

The real part of the impermeability tensor $[B_{ij}]$ for optically active liquids in the presence of an electric field **E** [6]. For all the groups included in the table $q_{66} = ½(q_{11} − q_{12})$

$\mathrm{Re}[B_{ij}] = B_{ij}^{(0)} + r_{ijk}E_k + q_{ijkl}E_kE_l + \ldots$		
Natural linear birefringence $B_{ij}^{(0)}$	Linear electro-optic r_{ijk}	Quadratic electro-optic q_{ijkl}
∞∞ Curie group		
$\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & 0 \\ 0 & 0 & n_{01}^{-2} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} q_{11} & q_{12} & q_{12} & 0 & 0 & 0 \\ q_{12} & q_{11} & q_{12} & 0 & 0 & 0 \\ q_{12} & q_{12} & q_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{44} \end{bmatrix}$
∞2 Curie group		
$\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & 0 \\ 0 & 0 & n_{03}^{-2} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ r_{41} & 0 & 0 \\ 0 & -r_{41} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} q_{11} & q_{12} & q_{13} & 0 & 0 & 0 \\ q_{12} & q_{11} & q_{13} & 0 & 0 & 0 \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{66} \end{bmatrix}$
∞ Curie group		
$\begin{bmatrix} n_{01}^{-2} & 0 & 0 \\ 0 & n_{01}^{-2} & 0 \\ 0 & 0 & n_{03}^{-2} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & r_{13} \\ 0 & 0 & r_{13} \\ 0 & 0 & r_{33} \\ r_{41} & r_{51} & 0 \\ r_{51} & -r_{41} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} q_{11} & q_{12} & q_{13} & 0 & 0 & q_{16} \\ q_{12} & q_{11} & q_{13} & 0 & 0 & -q_{16} \\ q_{31} & q_{31} & q_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & q_{44} & q_{45} & 0 \\ 0 & 0 & 0 & -q_{45} & q_{44} & 0 \\ -q_{16} & q_{16} & 0 & 0 & 0 & q_{66} \end{bmatrix}$

Table 2

The gyration tensor $[g_{ij}]$ for optically active liquids in the presence of an electric field **E** [6]. For all the groups included in the table $\beta_{66} = ½(\beta_{11} - \beta_{12})$

$g_{ij} = g_{ij}^{(0)} + \gamma_{ijk}E_k + \beta_{ijkl}E_kE_l + \ldots$		
Natural optical activity $g_{ij}^{(0)}$	Linear electrogyration γ_{ijk}	Quadratic electrogyration β_{ijkl}
$\infty\infty$ Curie group		
$\begin{bmatrix} g_{11}^{(0)} & 0 & 0 \\ 0 & g_{11}^{(0)} & 0 \\ 0 & 0 & g_{11}^{(0)} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} \beta_{11} & \beta_{12} & \beta_{12} & 0 & 0 & 0 \\ \beta_{12} & \beta_{11} & \beta_{12} & 0 & 0 & 0 \\ \beta_{12} & \beta_{12} & \beta_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{44} \end{bmatrix}$
$\infty 2$ Curie group		
$\begin{bmatrix} g_{11}^{(0)} & 0 & 0 \\ 0 & g_{11}^{(0)} & 0 \\ 0 & 0 & g_{33}^{(0)} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \gamma_{41} & 0 & 0 \\ 0 & -\gamma_{41} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} \beta_{11} & \beta_{12} & \beta_{13} & 0 & 0 & 0 \\ \beta_{12} & \beta_{11} & \beta_{13} & 0 & 0 & 0 \\ \beta_{31} & \beta_{31} & \beta_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_{66} \end{bmatrix}$
∞ Curie group		
$\begin{bmatrix} g_{11}^{(0)} & 0 & 0 \\ 0 & g_{11}^{(0)} & 0 \\ 0 & 0 & g_{33}^{(0)} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & \gamma_{13} \\ 0 & 0 & \gamma_{13} \\ 0 & 0 & \gamma_{33} \\ \gamma_{41} & \gamma_{51} & 0 \\ \gamma_{51} & -\gamma_{41} & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} \beta_{11} & \beta_{12} & \beta_{13} & 0 & 0 & \beta_{16} \\ \beta_{12} & \beta_{11} & \beta_{13} & 0 & 0 & -\beta_{16} \\ \beta_{31} & \beta_{31} & \beta_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_{44} & \beta_{45} & 0 \\ 0 & 0 & 0 & -\beta_{45} & \beta_{44} & 0 \\ -\beta_{16} & \beta_{16} & 0 & 0 & 0 & \beta_{66} \end{bmatrix}$

The total [B'] tensor derived from Eqs. (1)-(5) and transformed to the $X'Y'Z'$ coordinates has the following form dependent on the Curie group:
1) the ∞∞ symmetry

$$[B'] = \begin{bmatrix} n_{01}^{-2} + q_{11}E^2 & B'_{12} & 0 \\ -B'_{12} & n_{01}^{-2} + q_{12}E^2 & 0 \\ 0 & 0 & n_{01}^{-2} + q_{12}E^2 \end{bmatrix},$$

$$B'_{12} = i\, n_{01}^{-4}\left(g_{11}^{(0)} + \beta_{12}E^2\right) + i\, n_{01}^{-2} g_{11}^{(0)}\left(q_{11} + q_{12}\right)E^2, \tag{6}$$

2) the ∞2 symmetry

$$[B'] = \begin{bmatrix} n_{03}^{-2} + q_{33}E^2 & B'_{12} & 0 \\ -B'_{12} & n_{01}^{-2} + q_{13}E^2 & 0 \\ 0 & 0 & n_{03}^{-2} + q_{13}E^2 \end{bmatrix},$$

$$B'_{12} = i\, n_{01}^{-2} n_{03}^{-2}\left(g_{11}^{(0)} + \beta_{13}E^2\right) + i\, g_{11}^{(0)}\left(n_{01}^{-2}q_{33} + n_{03}^{-2}q_{13}\right)E^2, \tag{7}$$

3) the ∞ symmetry

$$[B'] = \begin{bmatrix} n_{03}^{-2} + r_{33}E + q_{33}E^2 & B'_{12} & 0 \\ -B'_{12} & n_{01}^{-2} + r_{13}E + q_{13}E^2 & 0 \\ 0 & 0 & n_{03}^{-2} + r_{13}E + q_{13}E^2 \end{bmatrix},$$

$$\begin{aligned} B'_{12} = {} & i\, n_{01}^{-2} n_{03}^{-2}\left(g_{11}^{(0)} + \gamma_{13}E + \beta_{13}E^2\right) + i\left(g_{11}^{(0)} + \gamma_{13}E\right)\left(n_{01}^{-2}r_{33} + n_{03}^{-2}r_{13}\right)E + \\ & + i\, g_{11}^{(0)}\left(n_{01}^{-2}q_{33} + n_{03}^{-2}q_{13} + r_{13}r_{33}\right)E^2, \end{aligned} \tag{8}$$

where the contribution of the products of $g_{11}^{(0)}$ and electro-optic coefficients is negligible compared to the products of n_{01}^{-2}, n_{03}^{-2} and the electrogyration coefficients.

2.2. Light modulation in measurement system

The intensity of the light emerging from the system of plane-parallel plates has been derived using the Jones calculus. To describe the transition of the light through a single plate we have used one of the most general forms of the Jones M-matrix, valid for any dichroic homogeneous elliptically birefringent medium, which has been derived by Ścierski & Ratajczyk [7]. The matrix was originally written with the use of variables that characterize the polarization of the light waves propagating in the medium. Next, the matrix written in the form explicitly depending on the [B] complex Hermitian tensor has been presented recently in Ref. [8].

Let us consider a typical experimental setup for the measurements of electro-optic coefficients based on the optical polarimetric method, which consists of the following elements arranged in the following order: a linear polarizer of the azimuth $\alpha_p = \pm 45°$ (relative to $+X'$ axis, which defines the reference zero azimuth), a quarter-wave plate of the azimuth $\alpha_{\lambda/4} = 0°$ or $90°$ (for the fast wave), a cuvette with an optically active liquid and immersed electrodes, and a linear analyzer of any arbitrary azimuth α_a. The intensity I of the light passing through the system relative to the intensity I_p behind the polarizer derived by the Jones calculus may be written as:

$$\begin{aligned}\frac{I}{I_p} &= \tfrac{1}{4}\left(T_f^2 + T_s^2\right) + \\ &+ \tfrac{1}{4}\left(T_f^2 - T_s^2\right)\frac{(B'_{11} - B'_{22})\cos(2\alpha_a) \pm z\,2\,\mathrm{Im}[B'_{12}]}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}} + \\ &\pm z\,\tfrac{1}{2}\cos(2\alpha_a)\frac{(B'_{11} - B'_{22})\,\mathrm{Im}[B'_{12}]}{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}\left(T_f^2 + T_s^2 - 2T_f T_s \cos\Gamma\right) + \\ &\mp z\,\tfrac{1}{2}\sin(2\alpha_a) T_f T_s \frac{B'_{11} - B'_{22}}{\sqrt{(B'_{11} - B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}\sin\Gamma,\end{aligned} \tag{9}$$

where the symbol * indicates the complex conjugate, the upper signs in the "$\mp$" and "$\pm$" symbols correspond to $\alpha_p = +45°$ and the lower signs to $\alpha_p = -45°$, $z = +1$ for $\alpha_{\lambda/4} = 0°$ and $z = -1$ for $90°$, T_f and T_s are the amplitude transmission coefficients for the fast and slow waves, respectively, and Γ is the phase difference between the slow and fast waves. It can be seen from Eq. (9) that turning the polarizer between the azimuths $+45°$ and $-45°$ gives an equivalent effect as changing $\alpha_{\lambda/4}$ between $0°$ and $90°$.

When the cuvette contains an optically active medium, the order of the quarter-wave plate and the cuvette is important. If the quarter-wave plate is placed behind the cuvette the following formula applies:

$$\begin{aligned}\frac{I}{I_{\mathrm{p}}} &= \tfrac{1}{4}\left(T_{\mathrm{f}}^2 + T_{\mathrm{s}}^2\right) + \\ &+ \tfrac{1}{4}\left(T_{\mathrm{f}}^2 - T_{\mathrm{s}}^2\right)\frac{(B'_{11}-B'_{22})\cos(2\alpha_{\mathrm{a}}) - 2z\,\mathrm{Im}[B'_{12}]\sin(2\alpha_{\mathrm{a}})}{\sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}} + \\ &\mp \cos(2\alpha_{\mathrm{a}})T_{\mathrm{f}}T_{\mathrm{s}}\frac{\mathrm{Im}[B'_{12}]}{\sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}\sin\Gamma + \\ &\mp z\,\tfrac{1}{2}\sin(2\alpha_{\mathrm{a}})T_{\mathrm{f}}T_{\mathrm{s}}\frac{B'_{11}-B'_{22}}{\sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}\sin\Gamma,\end{aligned} \tag{10}$$

where the upper and lower signs in "$\mp$" and the symbol z has the same meaning as in Eq. (9). In Eqs. (9) and (10) we omitted for brevity the terms containing $\mathrm{Re}[B'_{12}]$, which vanish for all forms of the $[B]$ tensor given by Eqs. (6)-(8). The phase difference in Eqs. (9) and (10) is given by

$$\Gamma = \frac{2\pi l}{\lambda}(n_{\mathrm{s}} - n_{\mathrm{f}}), \tag{11}$$

where λ is the wavelength of the light, l is the light path-length between electrodes in the cuvette, and n_{f} and n_{s} are the refractive indices of the fast and slow waves, respectively. The refractive indices of the liquid described by the complex Hermitian impermeability tensor can be found by employing the formulas [8]

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

$$n_{\mathrm{s}} = \sqrt{\frac{2}{B'_{11} + B'_{22} - \sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}}. \tag{13}$$

It is known from experiments that the difference between the field-free refractive indices n_{01}–n_{03} is very small in comparison to n_{01} and n_{03} (for castor oil between stainless steel plates at room temperature: $|n_{01}-n_{03}| \approx 1.6\cdot10^{-7}$ and $n_{01} \approx n_{03} \approx 1.48$ [3]), thus the expressions $n_{01}\,n_{03}$ and $n_{01} + n_{03}$ may be written using the average value $n_0 = (n_{01} + n_{03})/2$. Moreover, the relation $B'_{11} + B'_{22} >> \sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}$ enables the following approximations

$$\Gamma \approx \frac{2\sqrt{2}\,\pi l}{\lambda}\frac{\sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}}{(B'_{11}+B'_{22})^{3/2}} \approx \frac{\pi l\, n_0^3}{\lambda}\sqrt{(B'_{11}-B'_{22})^2 + 4B'_{12}B'^{*}_{12}}. \tag{14}$$

The transmissions T_f and T_s in Eqs. (9) and (10) depend on the length l according to the formulae

$$T_f^2 = \exp(-\kappa_f l), \quad T_s^2 = \exp(-\kappa_s l), \tag{15}$$

where κ_f and κ_s are the length-independent absorption coefficients. The difference $\kappa_f - \kappa_s$ is related with the relative difference in transmissions

$$(T_f - T_s)/\bar{T} = 2\tanh[-0.25(\kappa_f - \kappa_s)l], \tag{16}$$

where $\bar{T} = (T_f + T_s)/2$ is the average transmission coefficient. The absolute value $|(T_f - T_s)/\bar{T}|$ can be measured by the method outlined previously in Ref. [3]. The experimental value of $|(T_f - T_s)/\bar{T}|$ obtained for a given length l along with equation (16) allow us to find a value for any l. The other terms involving transmissions in Eq. (9) and (10) may be approximated as $T_f^2 + T_s^2 \approx 2\bar{T}^2$ and $T_f T_s \approx \bar{T}^2$, which allows for the reduction of $\bar{T}$ in further calculations of the modulation index.

It is worth noting that according to Eqs. (9) and (10) the natural optical activity of the liquid sample can not be compensated by rotations of the analyzer and the optimal conditions for measurements of electro-optic coefficients occur only for $\alpha_a = -45°$ and $+45°$. Two possible orientations of the polarizer, two orientations of the analyzer and two for the quarter-wave plate give eight combinations, which lead to four nonequivalent results either in equation (9) or (10). Each of these cases corresponds to different perturbations in electro-optic measurements by other unintended effects occurring at the same time.

3. RESULTS OF NUMERICAL CALCULATIONS

In the case of solid crystals the influence of imperfect crystal cutting and alignment on the accuracy of the measurements of the quadratic electro-optic coefficients is one of the major experimental problems. However, this source of errors becomes of little importance when measurements are performed for liquids, where the optic axis in the liquid spontaneously orients perpendicular to the plane of the electrodes and the linear birefringence $|n_{01}-n_{03}|$ is several orders of magnitude smaller than in crystals. Very low linear birefringence enables, however, a stronger manifestation of the optical activity and dichroism, even in directions far from the optic axis.

Let us consider in more detail the measurements of the $q_{13} - q_{33}$ effective coefficient in the castor oil using a sinusoidal modulating field $E = E_0 \sin(\omega t)$, which is directed perpendicular to the light beam. We assume that experimental data are typically processed employing the simplified formula that results from both Eqs. (9) and (10) for idealized conditions where the sample is isotropic ($n_{01} = n_{03}$), not dichroic ($T_f = T_s = T$), not optically active ($B'_{12} = 0$), and the phase difference Γ is so small that $\sin\Gamma \approx \Gamma$

$$|q_{13} - q_{33}| \approx \frac{2\lambda}{\pi l\, n_0^3} \frac{m_{2\omega}}{E_0^2}. \tag{17}$$

$m_{2\omega}$ in Eq. (17) is the modulation index defined as the ratio

$$m_{2\omega} = I_{2\omega} / I_0, \tag{18}$$

where I_0 is the constant component of the transmitted light intensity I, and $I_{2\omega}$ is the intensity at the second harmonic of modulating field. In our example the values of I_0 and $I_{2\omega}$ are calculated using the exact formulas presented in Chapter 2 by employing the form of the $[B']$ tensor for the ∞2 symmetry given in Eq. (7).

We used the following values published previously for the castor oil at room temperature obtained at λ = 632.8 nm: $n_0 = 1.48$, $|n_{01}-n_{03}| \approx 1.6\cdot10^{-7}$, $g_{11}^{(0)} = 2.2\cdot10^{-7}$ and $|(T_f - T_s)/\bar{T}| = 0.036$ given for l = 10 cm [3]. The effective electro-optic coefficient $|q_{33} - q_{13}| = 2\lambda K/n_0^3 \approx 5.8\cdot10^{-21}$ m^{2}V^{-2} was found by using the published value of the Kerr constant $K \approx 1.5\cdot10^{-14}$ mV^{-2} measured in the fresh castor oil at temperature 297 K [1]. Currently, there is a lack of data in the literature concerning the electrogyration in liquids which are not liquid crystals. Our initial results, which are not published yet, show, however, that the β_{31} coefficient in the castor oil is of the order of 10^{-23} m^{2}V^{-2}. Thus the electrogyration effect is negligible when the quadratic electro-optic effect manifests itself at the same time.

Considering the impact of undesirable effects on measurements of the effective coefficient $g_{ef} = |q_{33} - q_{13}|$, we use the following relative error

$$\Delta \approx 100\% \cdot (g_{ef} - g_{ef}^{id}) / g_{ef}^{id}, \tag{19}$$

where g_{ef} is the inaccurate value determined from the simplified equation (17) and g_{ef}^{id} is the ideal value, which is assumed in advance in our numerical analysis. The results of calculations presented in Fig. 1 show that the error Δ depends significantly on the light path-length l, and the dependences is clearly different for four nonequivalent combinations of the azimuths α_a, α_p and $\alpha_{\lambda/4}$. We would like to emphasise that the smallest values of l does not guarantee the smallest errors. This result is a consequence of two proportionalities $T_f^2 - T_s^2 \sim l$ and $\sin\Gamma \sim l$, which are satisfied for the smallest values of l, where the term $T_f^2 - T_s^2$ in Eqs. (9) and (10) is related to the factors that disturb the measurement, and the term $\sin\Gamma$ is related to the expected contribution of the electro-optic effect to the modulation index $m_{2\omega}$. The next important source of errors is related to the non-linearity of the term sin Γ. Because of the linear and circular birefringence in the oil the constant part of Γ may reach the values for which the approximation $\sin(\Gamma) \approx \Gamma$ becomes insufficient for the length l of the order of centimetre.

Since the data $(T_f - T_s)/\overline{T}$, n_{01}–n_{03}, and $q_{33} - q_{13}$ are known only as absolute values, we can not assign the individual curves on Fig. 1 to the specific values of the azimuths α_a, α_p, and $\alpha_{\lambda/4}$. Regardless of the signs, we can always identify that pair of measurement series, for which the measurement errors are almost compensated in the results presented as the arithmetic mean of two series. A pair of suitable series are, for example, the series that differ in the azimuth of the quarter-wave $\alpha_{\lambda/4} = 0°$ or 90°, while the orientation of other components are the same. Moreover, the results suitable for averaging can also be obtained for different azimuths α_a or α_p, with the same azimuth $\alpha_{\lambda/4}$. If the quarter-wave plate is placed between the polarizer and the cuvette, the suitable series should differ only in the azimuth $\alpha_p = -45°$ and +45°, and if the quarter-wave plate is placed between the cuvette and the analyzer the suitable series should differ only in $\alpha_a = -45°$ and +45°.

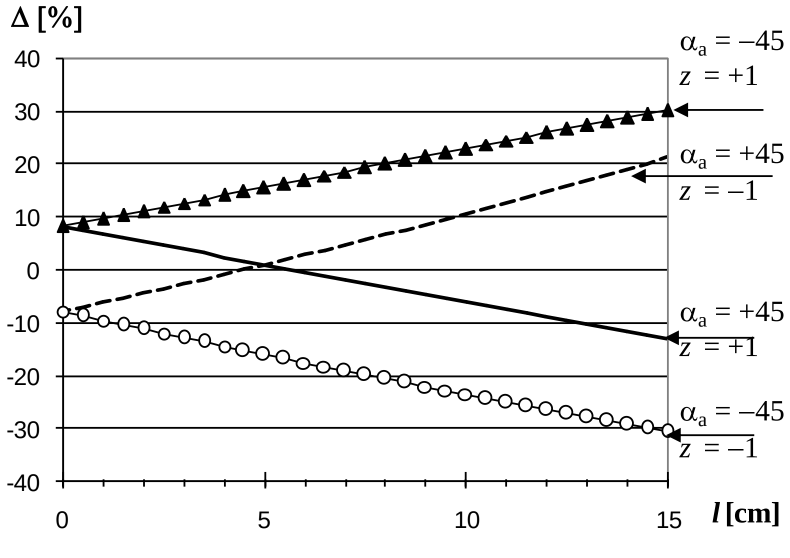

Fig. 1. The effect of the light path-length l on the relative error Δ [%] in the measurement of $|q_{13} - q_{33}|$ in the castor oil. The exemplary legend for the curves are given for the case when $\alpha_p = -45°$, the sign of $(T_f - T_s)/\overline{T}$, n_{01}–n_{03}, and $q_{33} - q_{13}$ are positive, and the quarter-wave plate is placed behind the cuvette

4. CONCLUSIONS

The analysis presented in this work shows that the optical polarimetric method enables the measurements of electro-optic coefficients in optically active liquids, but the measurable coefficients depends on the symmetry of the sample of liquid. In the case of isotropic liquid with the ∞∞ internal symmetry the effective coefficient $q_{11} - q_{12}$ of the quadratic electro-optic effect can be measured, which is equivalent to $q_{13} - q_{33}$.

The transition to the ∞2 symmetry observed e.g. in the castor oil placed between plane-parallel electrodes is associated with the permission for the linear electro-optic and linear electro-gyration effects and with the inequality $q_{11} - q_{12} \neq q_{13} - q_{33}$ (see Tables 1 and 2). However, the both linear effects and the quadratic one described by $q_{11} - q_{12}$ cannot manifest themselves in the observed situation where the optic axis in the oil spontaneously orients in the direction perpendicular to the plane of the electrodes, and the only measurable coefficient is $q_{13} - q_{33}$. The deviation from the ∞∞ symmetry observed in the castor oil may be higher or lower depending on many factors such as the electrode material, temperature, and the intensity of an applied electric field. Thus, it is possible that the value of the $q_{13} - q_{33}$ coefficient measured in a given sample may depend on measurement conditions.

In the case of the ∞ symmetry the linear electro-optic effect described by the $r_{13} - r_{33}$ coefficient should be strongly manifested in the optical response of the measurement system. Currently the linear response has been not observed in our measurements with liquids subjected to the sinusoidally varying field. Nevertheless, the ∞ symmetry should be reconsidered when the results for the static electric field would be available.

The example presented in Section 3 concerns the error analysis for the measurement of the effective quadratic electro-optic coefficient $|q_{13} - q_{33}|$ in the castor oil, which exhibits the symmetry ∞2 between a pair of plane-parallel electrodes. The numerical results obtained show that the measurements performed using the optical polarimetric method are sensitive to the influence of some undesired effects, such as the dichroism, natural linear birefringence, and natural optical activity, while the activity induced by an applied electric field (electrogyration effect) seems to be negligible. The measurement error significantly depends on the path-length of the light in the oil, but the shortest lengths do not guarantee the smallest measurement error. The contribution of undesirable effects can be mostly reduced in the results presented as an arithmetic mean of the two measurement series, which differ e.g. in the orientation of the quarter-wave plate.

REFERENCES

[1] **Stępień M., Ledzion R., Górski P., Kucharczyk W.**, Sci. Bull. of the Lodz University of Technology, s. Physics, **33** (2012) 89.
[2] Castor oil for research purposes from Sigma-Aldrich, Specification Sheet, product number 259853 (available at www.sigmaaldrich.com).
[3] **Izdebski M., Ledzion R., Górski P.**, Sci. Bull. of the Lodz University of Technology, s. Physics, **33** (2012) 39.
[4] **Tomkins H.G., Irene E.A.**, Handbook of Ellipsometry, William Anderw, 2005, p. 121.
[5] **Maldonaldo T.A., Gaylord T.K.**, Appl. Opt., **28** (1989) 2075.
[6] **Sirotin Yu.I., Shaskolskaya M.P.**, Fundamentals of crystal physics, Mir Publishers, 1982.
[7] **Ścierski J., Ratajczyk F.**, Optik (Stuttgart), **68** (1984) 121.
[8] **Izdebski M.**, J. Appl. Cryst., **45** (2012) 950.

ANALIZA POMIARU KWADRATOWEGO EFEKTU ELEKTROOPTYCZNEGO W OLEJU RYCYNOWYM

Streszczenie

Przedstawiono rozszerzoną teoretyczną analizę odpowiedzi układu pomiarowego na przyłożone pole elektryczne podczas pomiarów współczynników efektu elektrooptycznego w cieczy aktywnej optycznie metodą polaryzacyjno-optyczną. Analiza obejmuje ciecze o symetriach wewnętrznych opisanych grupami Curie $\infty\infty$, $\infty 2$ oraz ∞ i uwzględnia następujące zjawiska: naturalna aktywność optyczna, naturalna dwójłomność liniowa, dichroizm oraz efekty indukowane przez przyłożone pole elektryczne – liniowy i kwadratowy efekt elektrooptyczny oraz liniowa i kwadratowa elektrożyracja. Przedstawiony przykład dotyczy numerycznej analizy błędu pomiaru kwadratowego efektu elektrooptycznego w oleju rycynowym, który wykazuje symetrię $\infty 2$ po umieszczeniu go pomiędzy płasko-równoległymi elektrodami.