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STUDY OF ELECTRICALLY INDUCED ORIENTATIONAL ORDERING IN MINERAL OILS ON THE EXAMPLE OF ORLEN OIL TRAF0 EN

Abstract: A simple model of orientational ordering of molecules in the liquid under the influence of an applied sinusoidal electric field of low frequency is presented. The predicted theoretical dependencies of linear birefringence and light transmission coefficients on the intensity of the applied field were confirmed by experimental data obtained for transformer oil ORLEN OIL TRAF0 EN. It was found that the intensity of orientational effects in the oil depends strongly not only on the current conditions, but also on the thermal history of the sample. Furthermore it is shown that the minimum amount of dissolved contaminants (e.g. polyethylene) strongly increases the effects. The results suggest that it is necessary to reconsider the techniques for measuring the Kerr effect in liquids associated with deformation of electron cloud, because the traditional approach does not take into account the orientational effects occurring simultaneously with the Kerr effect.

Keywords: orientational ordering, mineral oil, polarimetric technique, low birefringence liquid, linear dichroism.

1. INTRODUCTION

An electro-optic effect is defined as a change in the optical properties of a material medium due to an applied electric field E which varies slowly compared with the frequency of light [1,2]. Traditionally, this phenomenon is considered as a change in refractive indices Δn or the components of dielectric impermeability tensor $[B_{ij}]$ resulting from deformation in the electron cloud and is divided into: (1) Pockels effect with the linear relationship i.e. $\Delta n \sim E$, (2)

Kerr effect with the quadratic relationship i.e. $\Delta n \sim E^2$, and (3) other effects of higher orders. Moreover, in liquids and gases, reorientation of the molecules in an electric field may lead to significant changes in the refractive indices and/or the absorption of light. This mechanism, however, does not lead to any simple relationship of the type $\Delta n \sim E^n$ and requires a fundamentally different description.

The orientational effects have not been taken into account in many earlier works related to the Kerr effect in various vegetable, mineral and synthetic oils which contain molecules with long carbon chains (see e.g. Refs. [3-8]). However, the measurement techniques used previously do not guarantee correct results for electronic electro-optic constants when orientational effects introduce significant phase shift in measured sample and/or changes in light transmittance. Therefore, there is a need to estimate the limitations of traditional measurement techniques and to develop new, more general methods in the future.

The aim of this paper is to present a simple statistical model of orientational ordering in an applied alternating electric field and its experimental verification on the example of transformer oil ORLEN OIL TRAF0 EN. The results are used to discuss the consequences for measurements of the Kerr constant using optical polarimetric method.

2. THEORETICAL ANALYSIS

2.1. Internal symmetry of transformer oil between electrodes

Changes in orientational ordering occur relatively slowly in comparison to the processes associated with deformations of the electron cloud. Thus, ordering of an initially isotropic liquid can be considered as a transition to the new lower internal symmetry. In the case of optically inactive liquids, the symmetry of disordered liquids is described by the $\infty\infty m$ Curie group while more or less ordered liquids have one of the symmetries: ∞/m , ∞m and ∞/mm [1,2]. When orientational ordering is caused by an alternating electric field with no DC component (as in our experiment) the ∞m symmetry may be excluded. Moreover, the optical Z axis of ordered liquids typically follows the direction of the applied electric field \mathbf{E} , which results in the same form of electric impermeability tensor for the other two ∞/m and ∞/mm symmetries, i.e.

$$[B] = \begin{bmatrix} n_{01}^{-2} + q_{13}E^2 & 0 & 0 \\ 0 & n_{01}^{-2} + q_{13}E^2 & 0 \\ 0 & 0 & n_{03}^{-2} + q_{33}E^2 \end{bmatrix}, \quad (1)$$

where slow orientational processes cause changes in major refractive indices n_{01} and n_{03} , while the quadratic electronic electro-optic effect is described by q_{ij} coefficients.

Let us consider the system, as in Refs. [3-8], where the electric field \mathbf{E} is applied perpendicularly to the direction of light propagation \mathbf{s} . It is convenient to introduce another coordinate system with the axes $Z''\|\mathbf{s}$ and $X''\|\mathbf{E}$ and in which the impermeability tensor has the form

$$[B'] = \begin{bmatrix} n_{03}^{-2} + q_{33}E^2 & 0 & 0 \\ 0 & n_{01}^{-2} + q_{13}E^2 & 0 \\ 0 & 0 & n_{01}^{-2} + q_{13}E^2 \end{bmatrix}. \quad (2)$$

The phase difference between the slow and fast waves in the liquid is given by

$$\Gamma = (2\pi l / \lambda)(n_s - n_f), \quad (3)$$

where n_s and n_f are the refractive indices of the slow and fast waves, respectively, λ is the wavelength of light and l is the path length. Because the components of tensor (2) satisfy the relation $B'_{11} + B'_{22} \gg |B'_{11} - B'_{22}|$ and $B'_{12} = 0$ we can write with a good approximation [9]

$$\Gamma \approx \frac{\pi l n_0^3}{\lambda} |B'_{11} - B'_{22}| \approx \frac{\pi l}{\lambda} |2(n_{01} - n_{03}) + n_0^3(q_{33} - q_{13})E^2|, \quad (4)$$

where n_0 is the average field-free refractive index $(n_{01} + n_{03})/2$.

2.2. Contribution of the Kerr effect to DC phase shift

In many works, quadratic electro-optic effect is described by the Kerr constant K defined as

$$\Delta n = \lambda K E^2. \quad (5)$$

Comparison of Eqs. (4) and (5) shows that there exists a relationship

$$|K| \approx \frac{1}{2} \lambda^{-1} n_0^3 |q_{33} - q_{13}|. \quad (6)$$

In all our experiments a sinusoidal modulating field $E(t) = E_0 \sin(\omega t)$ has been applied, where the angular frequency ω was set to 2620 rad/s (417 Hz). Hence, from formula (6), it follows that the contribution of the Kerr effect to the phase shift is $\Gamma_K = \pi l K E_0^2 [1 - \cos(2\omega t)]$. Substituting $l = 5$ cm in our experiment, the maximum amplitude of the applied field $E_{0\max} = 1.3 \cdot 10^6$ V/m and the Kerr constant $K = 1.8 \cdot 10^{-15}$ mV⁻² [5] measured previously in a similar fresh transformer oil, one obtains the contribution of the Kerr effect to the DC component Γ_0 of the phase shift up to about 0.027 degrees. Such a weak contribution of the Kerr effect is insufficient to explain our experimental results

where the phase shift induced by an applied field is many times greater and a quadratic relation $\Gamma_0 \sim E_0^2$ is not satisfied.

2.3. Statistical description of orientational ordering in an electric field

According to the Lambert-Beer law the intensity $I(l)$ of the light beam passing through the sample along the Z' axis is given by

$$I(l) = I(0) \cdot 10^{-A}, \quad (7)$$

where A is the absorbance (also known as optical density) defined as

$$A = \varepsilon l C. \quad (8)$$

In Eq. (8) ε is molar extinction coefficient and C the concentration of light-scattering (absorbing) particles in the sample.

Absorption of visible light is associated with transitions of electrons to excited states. We assume that there is only one kind of transition possible in a given sample. For non-magnetic electrically neutral particles the rate of light absorption depends on the transition dipole moment $\boldsymbol{\mu}$ and it can be shown that the absorbance is proportional to the square of the projection of the $\boldsymbol{\mu}$ vector onto the light-wave electric field vector $\boldsymbol{\mathcal{E}}$ [10]

$$A \sim \mu^2 \cos^2 \theta, \quad (9)$$

where θ is the angle between the $\boldsymbol{\mu}$ and $\boldsymbol{\mathcal{E}}$ vectors.

When a low-frequency electric field \boldsymbol{E} is applied, the potential energy of the particle in the field is given by

$$U = \int_{\pi/2}^{\theta} |\mathbf{p}(\theta') \times \mathbf{E}| d\theta' = -\frac{1}{2} \alpha E^2 \cos^2 \theta, \quad (10)$$

where \mathbf{p} is the electric dipole moment induced by the field \boldsymbol{E}

$$p = \alpha E \cos \theta. \quad (11)$$

In our simple model we assume that $\mathbf{p} \parallel \boldsymbol{\mu}$ for a given particle and the vectors \mathbf{p} and $\boldsymbol{\mu}$ are directed along the axis of the particle. However, a permanent dipole moment interacting with the field \boldsymbol{E} is not taken into account.

In the field \boldsymbol{E} the $\boldsymbol{\mu}$ vectors with the same probability density form a cone around the $\boldsymbol{E} \parallel X'$ axis. Hence, square of the average projection of the $\boldsymbol{\mu}$ moments onto the X' axis yields the following absorbance for the polarization $\boldsymbol{\mathcal{E}} \parallel X'$:

$$A_{X'} = k \mu^2 \langle \cos^2 \theta \rangle \quad (12)$$

and the absorbance for the polarization $\boldsymbol{\mathcal{E}} \parallel Y'$

$$A_{Y'} = \frac{1}{2} k \mu^2 \langle \sin^2 \theta \rangle = \frac{1}{2} k \mu^2 (1 - \langle \cos^2 \theta \rangle). \quad (13)$$

In order to find the average value of squared cosine of the θ angle we follow the Kielich's model of macromolecules reoriented by an AC electric field [11,12]

$$\langle \cos^2 \theta \rangle = \frac{\int N(U) \cos^2(\theta) d\Omega}{\int N(U) d\Omega}, \quad (14)$$

where the integration is performed over all solid angles $d\Omega$ between two cones whose half angles are θ and $\theta + d\theta$, i.e.

$$d\Omega = \sin(\theta) d\theta. \quad (15)$$

The energy distribution of electric dipoles in an electric field is traditionally described by the Boltzmann's distribution:

$$N(U) = N_0 \exp(-U/k_B T). \quad (16)$$

Collecting together Eqs. (10), (11) and (14)-(16) we have:

$$\langle \cos^2 \theta \rangle = \frac{\int_{-1}^1 \exp(s^2 x) s^2 ds}{\int_{-1}^1 \exp(s^2 x) ds} = (2x)^{-1} \left\{ e^x \left[\sum_{k=0}^{\infty} \frac{x^k}{(2k+1)k!} \right]^{-1} - 1 \right\}, \quad (17)$$

where $s = \cos\theta$ and $x = \alpha E^2/2k_B T$ are new variables.

Since attenuation of light beam in the oil sample is caused by various molecules, we separated the total measured absorbance into the absorbance dependent on the polarization of light and the isotropic absorbance A_{izo}

$$A_{X'} + A_{izo} = -\log T_{X'}^2, \quad (18)$$

$$A_{Y'} + A_{izo} = -\log T_{Y'}^2, \quad (19)$$

where $T_{X'}^2$ and $T_{Y'}^2$ are the amplitude transmission coefficients defined as the ratio $I(l)/I(0)$ for the X' and Y' polarization, respectively. In practice, the light intensities $I(0)$ and $I(l)$ inside the oil sample are not directly available for measurement. Therefore, we measured the overall transmission I/I_{in} through the system comprising the oil sample together with other optical elements such as half-mirror, polarizers, cuvette and quartz windows in the measuring chamber. Then we divide this transmission by the transmission I^*/I_{in}^* measured for the system with an empty cuvette and the same orientation of polarizers

$$T_{X'}^2, \text{ or } T_{Y'}^2 = \frac{I/I_{in}}{I^*/I_{in}^*}. \quad (20)$$

As seen from Eqs. (18) and (19), the linear dichroism may be described by an expression independent of isotropic absorbance, i.e.

$$\log \frac{T_{Y'}^2}{T_{X'}^2} = k \mu^2 \Phi, \quad (21)$$

where $\Phi = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2}$ is the orientational order parameter. Moreover, the isotropic absorbance may be determined independently of the dichroism with an accuracy to the constant factor $k\mu^2/3$

$$A_{izo} = -\log(T_{X'}^{2/3} T_{Y'}^{4/3}) - \frac{1}{3} k\mu^2. \quad (22)$$

The induced linear birefringence resulting from orientational ordering of the particles in an applied electric field is proportional to the parameter Φ [11-13]. Hence, the slowly varying DC component of the phase difference may be written as

$$\Gamma_0 = \Gamma_s \Phi + \Gamma_c, \quad (23)$$

where Γ_s is the phase shift at saturation state ($x \rightarrow \infty$) and a constant phase shift Γ_c was added to take into account the influence of other elements in the optical path, e.g. a quartz cuvette. The similar form of Eqs. (21) and (23) allows easy comparison of the two effects of different nature but having a common source in orientational ordering of the molecules in an applied electric field.

At weak fields $x \ll 1$ the $\Phi(E)$ dependency is nearly a quadratic function [13]

$$\Phi \approx \frac{2}{15} x = \frac{1}{15} \frac{\alpha}{k_B T} E^2 \quad (24)$$

and the Kerr constant may be calculated. When the values of Γ_s and $\alpha/2k_B T$ are found by fitting the theoretical expressions to experimental data, the Kerr constant defined as in formula (5), but now related to orientational mechanism, is given by

$$K' = \frac{\Gamma_s [\text{rad}]}{15\pi l} \frac{\alpha}{2k_B T}. \quad (25)$$

2.4. Transmission of light beam through measurement system

Let us consider an optical system composed of an ideal polarizer, homogeneous dichroic and linearly birefringent medium and an ideal analyzer. We describe the system in $X'Y'Z'$ coordinates where light propagates along the $+Z'$ axis and the X' axis is the optical axis in the liquid induced due to an orientational ordering in the field \mathbf{E} . The azimuth of the polarizer α_p and analyzer α_a will be given relative to the $+X'$ axis selected as a reference zero azimuth. The transmission of the light beam through the system can be found using, for example, Jones matrix calculus with the general form of the Jones M-matrix derived by Ściarski and Ratajczyk [14,15]. In particular, for $\alpha_a = 45^\circ$

and $\alpha_p = 315^\circ$ or $\alpha_a = 315^\circ$ and $\alpha_p = 45^\circ$ the ratio of the intensity of outgoing light I to the intensity I_p immediately after the polarizer is given by the formula

$$(I/I_p)_\perp = \frac{1}{4}(T_f^2 + T_s^2 - 2T_f T_s \cos\Gamma), \quad (26)$$

where T_f and T_s are the amplitude transmission coefficients for the fast and slow waves, respectively. Similarly, for the next configuration $\alpha_a = \alpha_p = 315^\circ$ or $\alpha_a = \alpha_p = 45^\circ$

$$(I/I_p)_\parallel = \frac{1}{4}(T_f^2 + T_s^2 + 2T_f T_s \cos\Gamma). \quad (27)$$

The values of I , T_f , T_s and Γ can always be decomposed into DC components I_0 , T_{f0} , T_{s0} , Γ_0 ; the components measured at modulating frequency ω ; the components at the second harmonic 2ω , etc. In particular Eqs. (26) and (27) allow to find

$$|\Gamma_0| = \arccos\left(\frac{T_f^2 + T_s^2}{2T_f T_s} \frac{I_{0\parallel} - I_{0\perp}}{I_{0\parallel} + I_{0\perp}}\right). \quad (28)$$

The transmissions T_f and T_s can be measured directly, but it requires another two configurations $\alpha_a = \alpha_p = 0^\circ$ and $\alpha_a = \alpha_p = 90^\circ$. As we are unable to distinguish between the fast and slow waves, we will use the symbols $T_{X'}$ and $T_{Y'}$ and it must always be true that $T_{X'} = T_f$ and $T_{Y'} = T_s$ or $T_{X'} = T_s$ and $T_{Y'} = T_f$ such that

$$I/I_p = \begin{cases} T_{X'}^2 & \text{for } \alpha_p = \alpha_a = 0^\circ, \\ T_{Y'}^2 & \text{for } \alpha_p = \alpha_a = 90^\circ. \end{cases} \quad (29)$$

Therefore, if the transmissions T_f and T_s change significantly with the applied field, it should be possible to measure non-zero values of I_ω and $I_{2\omega}$.

3. EXPERIMENTAL

A sample of ORLEN OIL TRAF0 EN was poured into a quartz cuvette. It is an insulating oil obtained from highly refined petroleum oil fraction. The oil does not contain oxidation inhibitors, metal passivators and others additives. The oil has very good electrical insulating properties, such as high breakdown voltage and low dielectric losses. Moreover, it has a high resistance to thermo-oxidation and has good stability in the electric field [16].

All components that come into contact with the oil were carefully cleaned with butyl acetate before the experiment. A pair of plane-parallel electrodes immersed in the oil were made of stainless steel. The electrodes were kept at a precise distance of $d = 4.12$ mm by the separators made of Teflon. The length of

the electrodes $l = 49.2$ mm was almost equal to the length 50 mm of cuvette. The cuvette with the oil and electrodes was placed into the measurement chamber.

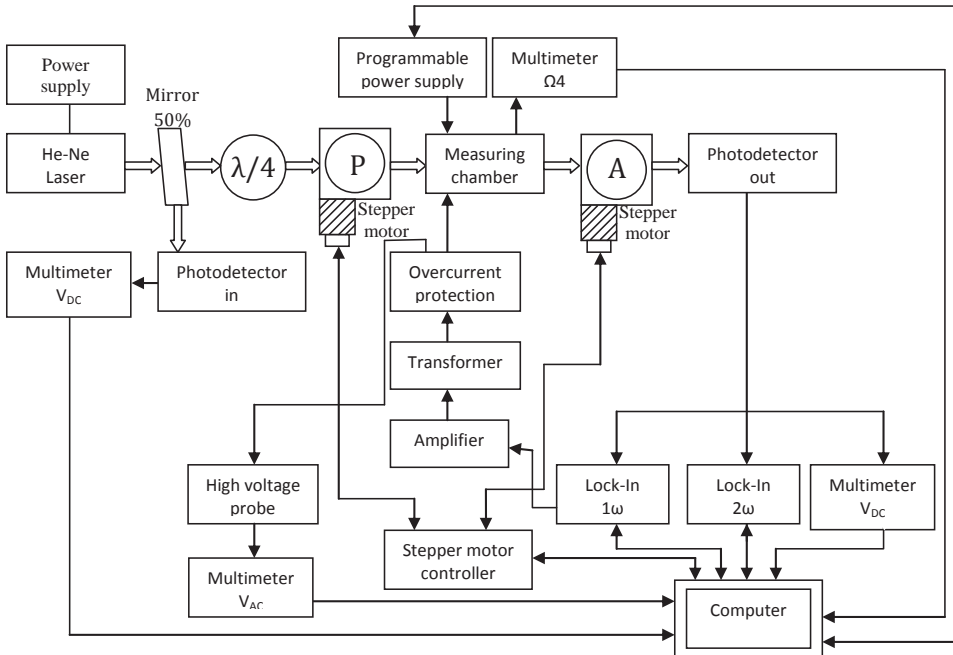


Fig. 1. The experimental setup

The experimental setup used in our measurements is presented in Fig. 1. A light beam of wavelength $\lambda = 632.8$ nm from the He-Ne laser falls on the half-mirror, where it is divided into two beams. One of them falls on the photodetector Thorlabs PDA36A–EC connected to KEITHEY 2000 digital multimeter working as a DC voltmeter, while the second beam falls on the quarter-wave plate manufactured by Melles Griot. After passing through the retardation plate the beam passes through the Polaroid polarizer P, then through the measuring chamber and the analyzer A. Afterwards the beam falls on the second photodetector Thorlabs PDA100A–EC. Three components of the signal from this photodetector were recorded: the DC component was measured by KEITHEY 2000 digital multimeter working as a DC voltmeter, the RMS voltages at the first and the second harmonic of modulating field were measured by two digital signal processing lock-in amplifiers produced by EG&G instruments, model 7265. The “ 1ω ” lock-in amplifier was also used for generating the modulating signal that was amplified by amplifier YAMAHA A-500 and passed through a transformer TSZ 90 VA TELTO in order to obtain

the voltages up to about 3700 V RMS. An over-current relay was added after the transformer for safety. The polarizer P and the analyzer A were rotated using Thorlabs NR360S/M stepper motors connected to Thorlabs BSC203 controller.

The measuring chamber was heated using 8 ceramic cement power resistors connected to MOTECH LPS-305 programmable power supply and the temperature was measured by KEITHEY 2700 digital multimeter with PT100 sensor. A computer program controlled the process of heating and cooling, the measurements and the data acquisition.

4. RESULTS AND DISCUSSION

A fresh transformer oil ORLEN OIL TRAF0 EN (www.orlenoil.pl) was poured directly from the original canister into a quartz cuvette and the electrodes were immersed in the oil. Before starting the measurements the oil in the cuvette was heated for 6 hours to a temperature of 25, 60, 70, 80 or 90°C (one temperature for one measurement series). After heating, the oil was cooled down for about 12 hours and all our measurements started after reaching room temperature 22...23°C. The alternating electric field between the electrodes was increased step by step from 0 up to about $9 \cdot 10^6$ V/m RMS including 40 different non-zero levels and after reaching the maximum intensity the field was reduced to zero in the reverse order. Thanks to the use of stepper motors controlled by the computer, measurements for several orientations of the polarizer and the analyzer were quickly made for each fixed level of the field strength. When the whole cycle including heating at a given temperature, cooling and measurements was completed, the cycle for another heating temperature began. Due to time-consuming procedure, our measurements were performed for only one frequency of the applied field $f = 417\text{Hz}$.

The results obtained for pure oil heated at various temperatures are shown in Figures 2 and 3. As one can see, the oil heated at temperatures T not exceeding 70°C exhibits nearly no linear birefringence nor linear dichroism induced by an applied electric field. However, the effects manifest themselves far stronger in the oil which was heated to temperature 80 or 90°C. The cuvette used in our measurements did not turn out to be neutral optically and the phase shift of 2.3...2.4 degrees visible on Fig. 2 for $E_{\text{RMS}} = 0$ corresponds to the shift measured for the empty cuvette.

The birefringence shown in Fig. 2 for $T = 70^\circ\text{C}$ is nearly proportional to the square of the field strength (excluding the offset introduced by the cuvette) and no saturation is visible. In the case of higher temperature of heating we can still observe a quadratic dependence in the area of weak field but a saturation is also

visible for higher field of order of 10^6 V/m. The values of the Kerr constant K' (25) and the saturation birefringence $\Delta n_s = \Gamma_s \lambda / (2\pi l)$ obtained by fitting the theoretical expressions from section 2.3 to experimental data are presented in Table 1.

Reorientation of molecules in a viscous oil is a rather slow process. With increasing values of E_{RMS} a time of about 2.5 h is required to obtain a good agreement between experimental data and theoretical $\Gamma(E_{\text{RMS}})$ dependency of Section 2.3. In contrast to this, a relaxation process observed with decreasing value of E_{RMS} is much slower, which can be seen particularly clearly in Fig. 2 for the data at $T = 90^\circ\text{C}$.

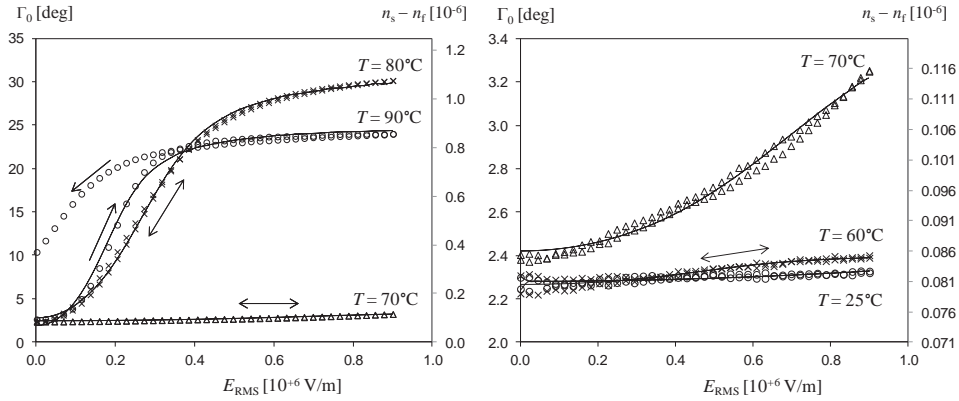


Fig. 2. Phase shift Γ_0 and corresponding linear birefringence $n_s - n_t = \Gamma_0 \lambda / (2\pi l)$ induced in pure oil sample as a function of field strength E_{RMS} . Interpolation was plotted according to Eqs. (23) and (17). For the data at $T = 90^\circ\text{C}$ the interpolation was limited to experimental data obtained for increasing intensity of the field

Table 1

The Kerr constant K' for orientational mechanism and the saturation birefringence Δn_s for pure oil at room temperature after heating at temperature T . The values of Δn_s are decoupled from the influence of the phase shift Γ_c in the cuvette

Temperature of heating T [$^\circ\text{C}$]	weak field K' [10^{-10} mV^{-2}]	saturation Δn_s [10^{-6}]
90	8.7	0.82
80	4.7	1.02
70	0.03	0.04
60	0.008	< 0.01
25	0.007	< 0.01

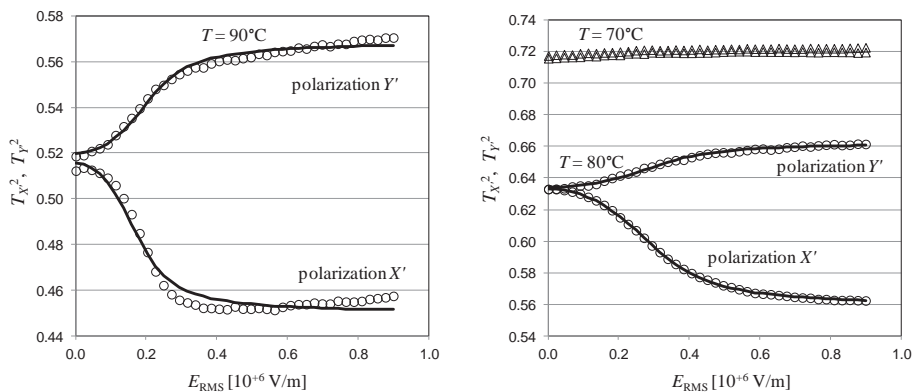


Fig. 3. Transmissions $T_{X'}^2$ and $T_{Y'}^2$ of light polarized in the X' and Y' plane as a function of the field strength E_{RMS} in pure oil. The graph shows only the results obtained for increasing values of E_{RSM} . Interpolation was plotted according to Eqs. (12), (13) and (17)-(19) for $A_{izo} = 0$

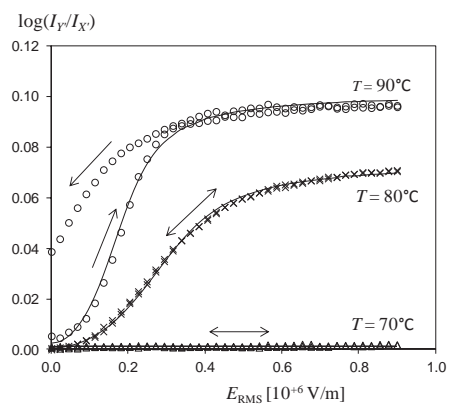


Fig. 4. Dependence of $\log(T_{X'}^2/T_{Y'}^2)$ term on field strength E_{RMS} obtained for the pure oil. Interpolation was plotted according to Eq. (21) together with Eq. (17)

Changes in the transmission of light due to reorientation of molecules in an applied electric field occur simultaneously with other changes which do not depend on polarization of the light nor the applied field, namely, the oil becomes less transparent during the heating and then returns slowly to its original transparency at room temperature. For this reason, the interpolation plotted in Fig. 3 for the data at $T = 90^\circ\text{C}$ does not fit well with the experimental data. Since we do not know the law describing the change in isotropic absorbance A_{izo} , we cannot compensate its influence on the T_X^2 and T_Y^2 transmissions. However, as we showed previously in Eq. (21), the term $\log(T_X^2/T_Y^2)$ does not depend on A_{izo} . For this reason the interpolation shown on Fig. 4 for the data at $T = 90^\circ\text{C}$ fits better than that in Fig. 3.

Eqs. (21) and (23) show that $\log(T_X^2/T_Y^2)$ and Γ depend on the order parameter Φ in the same manner. Consequently, their dependence should be linear, which is confirmed from the plots of Fig. 5.

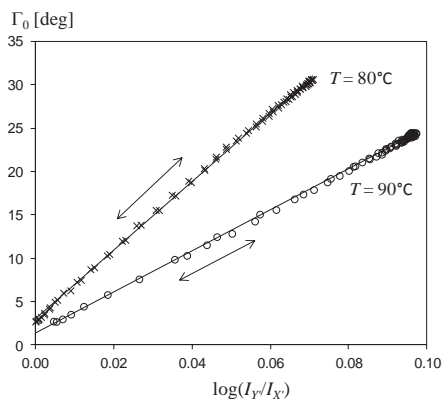


Fig. 5. Linear relationship between $\log(T_X^2/T_Y^2)$ term and phase shift Γ_0 plotted for the results shown in Figs. 2 and 4

It is worth noting that the effects resulting from the reorientation of molecules in an applied electric field may be much stronger after adding a small amount of impurities with long straight molecules. An example of the results obtained for the transformer oil with the addition of polyethylene is shown in Fig. 6.

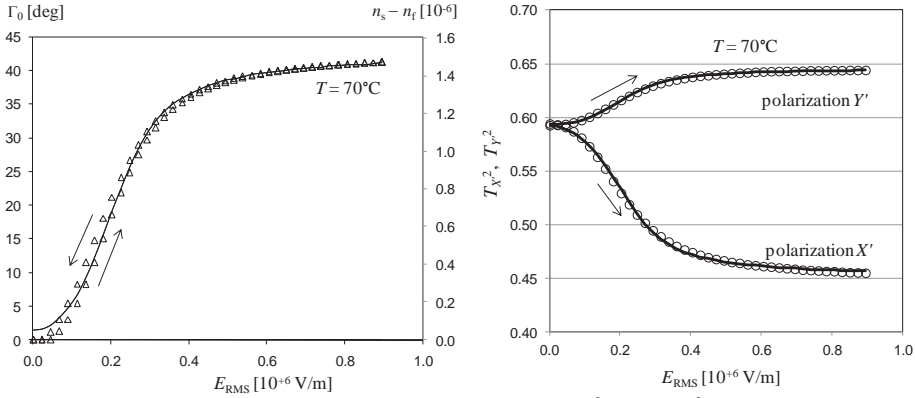


Fig. 6. Plots of phase shift Γ_0 and transmissions $T_{X'}^2$ and $T_{Y'}^2$ of light against field strength E_{RMS} for 10 g of transformer oil ORLEN OIL TRAF0 EN containing 0.04 g polyethylene which was partly dissolved in the oil during heating at 70°C

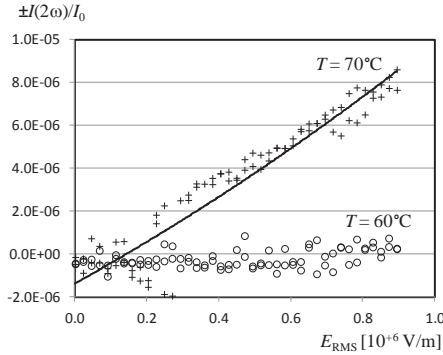


Fig. 7. Modulation depth $I(2\omega)/I_{in}$ measured as a function of field strength E_{RMS} at second harmonic of modulating signal of the frequency $f = 417$ Hz obtained for the oil with addition of polyethylene. Sign of phase $\varphi_{2\omega}$ is taken as the sign of $\pm I(2\omega)$. Configuration applied $\alpha_a = \alpha_p = 0^\circ$ excludes interference and contribution of the Kerr effect (see Eq. (29))

Reorientation of particles in an electric field is a very slow process in comparison with changes resulting from the electronic electro-optic effect. Thus, it can be expected that modulation of the transmission coefficients at the first or second harmonic of the modulating field should not be a significant effect when the Kerr constant is measured using the modulating field with a frequency of several hundreds of hertz. However, the addition of polyethylene results in a surprising modulation which we cannot explain as a manifestation of the Kerr

effect nor oscillations of the angle θ . The modulation manifests most strongly for the light polarized in the direction of the applied field X' . The modulation depth shown in Fig. 7 is a few percent of the depth occurring in a typical system for measuring the Kerr constant employing polarimetric technique with a quarter-wave retardation plate.

5. CONCLUSIONS

All materials show Kerr effect that originates from the deformation of electron cloud and its intensity may be considered as constant for a given chemical composition and temperature. In contrast to the electronic effects, the effects related to the reorientation of the molecules of liquid in an alternating electric field may or may not manifest itself clearly depending on the history of the sample. The electrically induced birefringence and dichroism observed in ORLEN OIL TRAF0 EN are strongest immediately after heating and cooling to room temperature and disappear after a time of a few weeks when we are no longer able to distinguish between samples with different thermal history. It should be noted, however, that the temperature $\leq 90^\circ\text{C}$ in our experimental setup could not cause significant changes in the chemical composition of the samples. The samples of the oil heated at various temperatures and cooled to room temperature show different dependence of the birefringence Δn and the light transmission coefficients $T_{X'}$ and $T_{Y'}$ on the electric field strength E . In the case of samples heated at temperature 80 or 90°C we can observe both the $\Delta n \sim E^2$ dependence for weak field (orientational Kerr effect) and the saturation for higher field of order of 10^6 V/m. The saturation was not reached for lower heating temperature.

The observed thermal activation of orientational effects in ORLEN OIL TRAF0 EN may result, for example, from the presence of a minimum amount of suspended solid particles which dissolve at a higher temperature and then are precipitated for a long time after cooling to the room temperature. Intensification of orientational effects after adding a small amount of polyethylene to the oil seems to confirm this hypothesis. However, it is also possible to formulate another hypothesis: ORLEN OIL TRAF0 EN typically contains 8% of water [16], which means that the hydrolysis and self-ionization of water leads to the formation of hydrogen bonds with the molecules of the oil and the number of bonds increases quickly with increasing temperature. The addition of polyethylene probably result in the formation of hydrogen bonds between the polyethylene chains at lower temperature than in the case of other oil particles.

Hydrogen bonds disappear during cooling but the slow rate of this process may be responsible for the memory effect observed in our experiment. Thus, the observed changes in orientational effects cannot be considered as a good measure of the quality of the oil, while the electronic Kerr constant reflects roughly the average composition of the sample.

The electronic Kerr effect in liquid is usually measured using polarimetric technique and some assumptions are traditionally applied to simplify the measurement procedure (compare e.g. Refs [3-8]):

1. The liquid does not introduce any phase shift with the exception of very small changes $\Delta\Gamma$ resulting from the electronic Kerr effect. Thus, according to Eqs. (26) and (27), the system with quarter-wave plate (where the total phase difference is $\Gamma = \Delta\Gamma \pm 90^\circ$) gives an almost linear relationship between I and $\Delta\Gamma$.
2. The transmission $T_f = T_s$ does not depend on the polarization of the light.
3. The T_f and T_s transmissions show no change with the applied field.

The results presented in this study show that all of the above assumptions may be questionable for some liquids. To the best of our knowledge, no method known from the literature is suitable for measurements of the Kerr effect where assumption 3 is not satisfied. Therefore, there is a need to develop a new, more general procedure for measuring the Kerr constant in liquids. When the traditional polarimetric method with static quarter-wave plate is still intended to be used for a liquid, assumptions 1-3, mentioned above, should be verified experimentally for the liquid prior to the measurements.

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BADANIE INDUKOWANEGO ELEKTRYCZNIE ORIENTACYJNEGO PORZĄDKOWANIA W OLEJACH MINERALNYCH NA PRZYKŁADZIE OLEJU TRANSFORMATOROWEGO ORLEN TRAF0 EN

Streszczenie

Przedstawiono prosty model orientacyjnego porządkowania molekuł cieczy pod wpływem przyłożonego sinusoidalnie zmiennego pola elektrycznego niskiej częstotliwości. Teoretyczne zależności liniowej dwójłomności oraz współczynników transmisji światła od natężenia przyłożonego pola zostały potwierdzone przez dane doświadczalne otrzymane dla oleju transformatorowego ORLEN TRAF0 EN. Stwierdzono, że intensywność efektów

orientacyjnych w tym oleju zależy silnie nie tylko od bieżących warunków, lecz także od termicznej historii próbki. Ponadto pokazano, że minimalny dodatek rozpuszczonych zanieczyszczeń (np. polietylenu) może zdecydowanie wzmocnić te efekty. Otrzymane wyniki sugerują, że należy ponownie rozważyć techniki pomiaru efektu Kerra w cieczach, związanego z deformacją chmury elektronowej, gdyż tradycyjne podejście nie uwzględnia efektów orientacyjnych, które występują jednocześnie z efektem Kerra.

