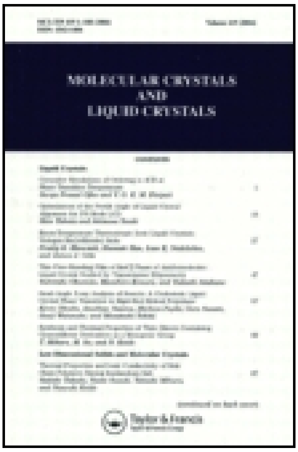

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KERR-EFFECT IN ISOTROPIC LIQUID PHASE OF MONOTROPIC NEMATOGENS

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Abstract The Kerr constant of two monotropic nematogens with different molecules length is measured. The low temperature of the nematic-isotropic liquid phase transition which is typical for monotropic LC created the conditions for the observation of two Kerr-effect dispersions at the frequency lower than 10 MHz. It was shown that the low frequency dispersion process is connected with cooperational orientational molecules motion whereas high frequency is connected with the rotation of the individual molecules of nematogen.

Keywords: Kerr-effect, birefringance, monotropic mesogener; phase transition, dispersion

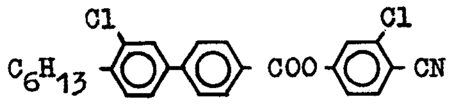
INTRODUCTION

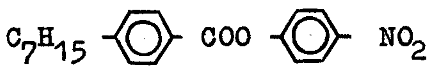
Considerable experimental material concerning the observations of the Kerr-effect in isotropic melts of enantiotropic LC has been accumulated in the last years[1-10].

The purpose of the present work is to study electro-optical properties of monotropic mesogens near the temperature of phase transition T_c from isotropic into nematic state. Lower temperatures of such transition (close to room temperatures) of monotropic LC are expecially important in studying relaxational phenomena in pretransitional temperature region.

EXPERIMENTAL

There were studied two monotropic nematic liquid crystals having the following molecular structure and temperatures of phase transitions:

A

K 74°C N (34.6°C) I

B

K 55°C N (34.9°C) I

Kerr-effect was studied by using two of the above described experimental methods[10-12].

Under the action of the electric field $E=E_0\cos 2\pi ft$, birefringence Δn appears in an isotropic melt

$$\Delta n = \frac{1}{2}[\overline{\Delta n} + \widetilde{\Delta n}\cos(4\pi ft - \delta)] \qquad (1)$$

Eq. (1) includes the constant (independent on time t) $\overline{\Delta n}$ and the harmonically changing component with the amplitude $\widetilde{\Delta n}$. Recording the light flux Φ which passes through the system of polarizer-Kerr cell-analyzer at different electric field frequencies, one can study the frequency dependence of both $\overline{\Delta n}$ and $\widetilde{\Delta n}$

$$\Phi \sim \overline{\Delta n}^2 + \frac{1}{2}\widetilde{\Delta n}^2 \qquad (2)$$

The Kerr-effect was also measured by the method of birefringence compensation using a rotational elliptical compensator[12]. In this method only the constant anisotropy component $\overline{\Delta n}$ is compensated. It enables us to measure the frequency dependence of $\overline{\Delta n}$ apart from $\widetilde{\Delta n}$. Electro-optical effect in this case is characterized by the Kerr constant $K = \overline{\Delta n}/E^2$. The measurements were carried out by using both methods at temperatures $T - T_c$ from 0.1 to 25°K.

RESULTS

The Kerr law was satisfied in the investigated substances at all temperatures and frequencies of electric field. The static values of Kerr constants K_0, which were measured at low frequency ($f < 200$ Hz) from the slope of experimental dependences $\overline{\Delta n} = \varphi(E^2)$, increases sharply in absolute value with the temperature approaching T_c. This is a consequence of increasing intensity of the order fluctuations. Temperature dependences of K_0 in the isotropic phase of the investigated monotropic samples can be approximated by Landau - de Gennes dependences $K_o \sim (T - T^*)^{-1}$ (Figure 1). It means that the thermodynamic laws of the static electro-optical properties of monotropic nematics do not differ from the corresponding laws, typical for enantiotropic liquid crystals near the N↔I phase transition.

Frequency dependences of relative light flux Φ_f/Φ_o for substances A and B are given in Figure 2. Value Φ_o is a flux at f<200 Hz. Strong dispersion Φ_f / Φ_o was found in the frequency range used. For each substances two frequency regions of the dispersion are typical: low frequency (LF) and high frequency (HF) dispersions with relaxation times τ_1 and τ_2 respectively. Figure 2 shows an important experimental fact. At the same temperature LF dispersion of substance A electrical birefringence appears at the frequencies two decades lower than substance B LF dispersion. The same difference can be seen in these substances for HF dispersion regions of Kerr-effect. Independent measurements of $\overline{\Delta n}$ with the rotational elliptical compensator showed only one dispersion region to be typical for $\overline{\Delta n}$. These frequencies correspond to HF dispersion Φ_f / Φ_o. The frequency dependences Φ_f / Φ_o and $\overline{\Delta n_f} / \overline{\Delta n_o}$ coincide wihtin adequate accuracy (Figure 2). However, at rather high frequencies, the relation $\overline{\Delta n_f} / \overline{\Delta n_o}$, unlike Φ_f / Φ_o, can change its positive sign into negative one. So the presented experimental data show that the HF dependence of the measured effect is a $\overline{\Delta n}$ dispersion whereas the LF one is likely to be caused by $\widetilde{\Delta n}$ dispersion.

The LF dispersion of the electric birefringence in pretransition temperatures region from isotropic into nematic phase in enantiotropic liquid crystals is a well studied phenomenon[3,4,8,10,16]. Orientational relaxation of dielectrically anisotropic "swarms" of axially oriented molecules, i.e. mesophase fluctuational nuclei, are responsible for this effect. Their sizes in the phase transition region can increase greatly as the temperature falls, and it is exhibited in a substantial dependence of time τ_1 on T. To analyze results obtained in this work for monotropic liquid crystals one can use the formula which connects the change of light flux constant component with the relaxation time τ_1 of LF electric birefringence dispersion[10]:

$$\frac{\Phi_f}{\Phi_o} = \frac{2}{3}\left(\frac{\overline{\Delta n_f}}{\overline{\Delta n_o}}\right)^2\left(1 + \frac{1}{2}\,\frac{1}{1 + 4\pi^2 f^2 \tau_1^2}\right) \qquad (3)$$

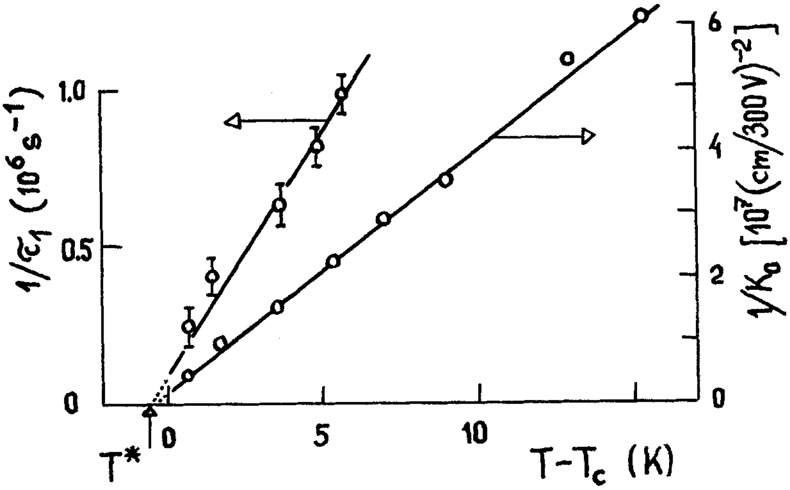


FIGURE 1 Temperature dependences of K_o^{-1} and τ_1^{-1} for substance B.

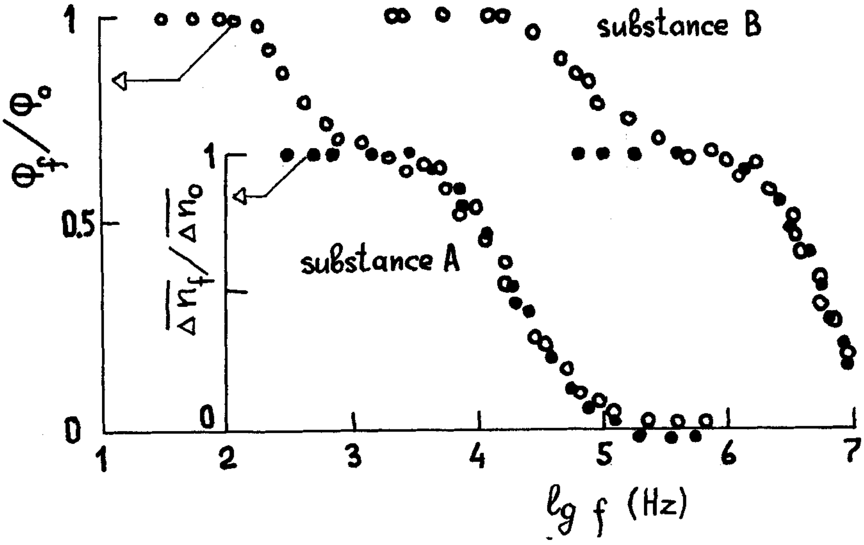


FIGURE 2 Frequency dependences of the light flux (white dots) and the birefringence (black dots). Temperature is 309 K.

Taking into consideration the fact that for the LF region $\overline{\Delta n_f} / \overline{\Delta n_o} = 1$ (Figure 2), the approximation by Eq. (3) of experimentally measured values φ_f / φ_o makes it possible to determine τ_1 of both substances. As an example, in the Figure 1 (a curve) it is given the temperature dependence $1/\tau_1$ of monotropic nematogen B. The same dependence is also obtained for nematogen A. It is typical for the relaxation of highly correlated molecules in the isotropic phase of enantiotropic LC investigated in the earlier works[3, 4, 10, 13]. In this case the LF dispersion in the isotropic phase can be connected with macroscopic viscosity parameters determined by molecules cooperational rotation in the pretransition temperatures region. A number of LC being experimented with, it was shown[13, 14] that the connection between dynamic parameters which are above and below the temperature of phase transition T_c can be quantitatively described by the following equation

$$\gamma_1 = \frac{9}{2}\tau_1(T - T^*)\frac{L}{T_c} \qquad (4)$$

where T^* is a temperature of fictitious phase transition; L is a latent melting heat; γ_1 is a rotational viscosity at the transition temperature. It was experimentally found that great difference of τ_1 for two investigated substances can in principle be depended on a number of factors according to (4). The Table gives parameters values contained in Eq. (4).

TABLE Physical parameters of the investigated samples.

Sample	L (erg/cm^3)	τ_1 (s)	$\tau_1(T-T^*)$ (s·°K)	γ_1 (P)	τ_2 (s)	η (P)
A	$42 \cdot 10^5$	$250 \cdot 10^{-6}$	$535 \cdot 10^{-6}$	32	$710 \cdot 10^{-8}$	44
B	$88 \cdot 10^5$	$2.8 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$	0.93	$3.2 \cdot 10^{-8}$	0.57

τ_1, τ_2 and η are measured at 309 K, γ_1 are calculated from Eq. (4).

Application of the given values $\tau_1(T - T^*)$, L and T_c makes it possible to obtain the value of rotational viscosities γ_1 of the investigated substances near the temperature of the phase transition. Thus found values γ_1 are also presented in the Table. They differ by a factor of thirty for A and B samples. So we may suppose that the main difference of LF relaxation times is determined by the pretransitional viscosity properties of monotropic nematics.

The HF dispersion of electric birefringence has been studied much less. The use of monotropic substances in this work for the first time enabled to measure the whole dispersion curve in the radiofrequency range and hence to obtain quantitative data of the relaxation time for HF dispersion τ_2 as well as the nature of their temperature dependence in the pretransition region. Experimental dependences $\Delta n = \varphi(f)$ (Figure 2) correspond to frequency dependences of dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ of the substances investigated in the nematic state[15-16]. This correspondence also includes the sign change from positive to negative at HF. It is well known that similar dependence $\Delta\varepsilon$ for LC with the positive dielectric anisotropy ($\varepsilon_{\parallel} > \varepsilon_{\perp}$) is connected with the relaxation of the longitudinal component of dielectric constant $\varepsilon_{\parallel}$ which is determined by the exclusion of rotation mechanism of polar molecules around a short cross axis from dipole polarization of LC. Therefore the experimental dependence $\overline{\Delta n}_f$ on the frequency as well as LF dispersion region of dielectric anisotropy of mesophase can be expressed by Debye formula:

$$\overline{\Delta n}_f = \overline{\Delta n}_\infty + \frac{\overline{\Delta n}_0 - \overline{\Delta n}_\infty}{1 + 4\pi^2 f^2 \tau_2^2} \qquad (5)$$

Quantitative correspondence of experimental dependences $\overline{\Delta n}_f$ on the theoretical curve frequency (5) enabled to determine times of HF dispersion of Kerr-effect τ_2. Thus obtained τ_2 values are presented in the Table and the corresponding temperature dependence τ_2 for A substance is given in Figure 3. Here are also given the temperature dependences of dielectric relaxation times in the isotropic liquid and LC (unbroken straight lines)[15]. The values τ_2 for the two investigated substances are different for more than 2 decades. It fully corresponds to the viscosities differences η for A and B (see Table) and to somewhat greater asymmetry of the first sample molecules form compa-

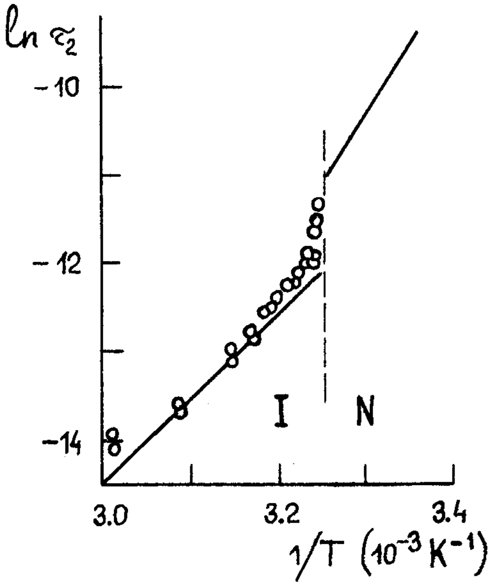


FIGURE 3 The relaxation time τ_2 of HF dispersion of the Kerr-effect (dots) in comparison wiht the dielectric relaxation time (lines) for substance A.

red with the second one. Molecular orientational dipole mechanism of Kerr-effect HF dispersion is as well confirmed not only by the quantitative coincidence of times of relaxation but also by the corresponding activation energies of 18 kcal/mol found from Kerr-effect dispersion and from the dielectric polarization. It should be noted that with the temperature decrease and its approximation to the temperature of isotropic nematic transition T_c, times τ_2 increase sharply, noticeably deflecting from the linear dependence which is typical for the isotropic phase far from T_c. It is apparently the consequence of increasing intensity of the orientational order fluctuations (mesophase nuclei). In these conditions polar molecules rotation around the cross axis requires overcoming an extra potential barrier which is typical for the substances in LC state.

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