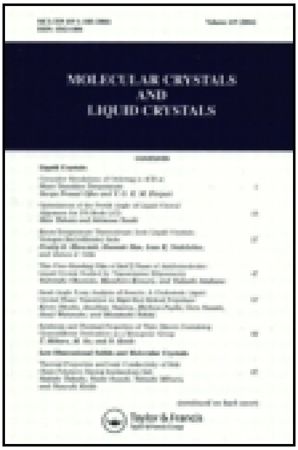

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Study of Elastic Constants of Cholesteric-Nematic Mixtures

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Study of Elastic Constants of Cholesteric–Nematic Mixtures

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We propose a technique for determining of elastic constants K_{22} and K_{33} of induced cholesterics, which is based on studies of the electro-optic characteristics of cholesteric–nematic transition, dielectric properties, and pitch of induced cholesterics. Instead of the linear approximation of experimental dependencies of the threshold fields, we propose to use the hyperbolic and parabolic approximations of experimental data to determine constants K_{22} and K_{33} with increased accuracy.

Keywords: cholesteric-nematic transition; elastic constants; liquid crystal mixtures

INTRODUCTION

Cholesteric–nematic mixtures (CNM) (or induced cholesterics) are among the most popular materials in modern optoelectronics. Due to the effect of selective reflection in cholesteric liquid crystal (LC) planar layers, they found applications in reflective liquid crystal displays (LCDs), and also in lasers with distributed feedback. Operation of a CNM-based LC device strongly depends on the set of physical parameters of the LC mixture.

The main challenges in creating of CNM-based devices are development of the LC mixtures with desired characteristics of selective reflection, high-quality surface stabilization of the LC layer, and development of new concepts for electronic control. This work is focused on solving the first of the above mentioned problems, in particular, on establishing the influence of the physical parameters and concentrations of CNM components on the final optical characteristics.

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This study will expand the possible applications of the selective reflection in induced cholesterics.

METHOD FOR DETERMINING OF ELASTIC CONSTANTS OF INDUCED CHOLESTERICS

Frank elastic constants influence the basic physical characteristics of induced cholesterics and, therefore, methods for determining of these constants have been investigated extensively [1–3]. Earlier we proposed the technique to determine the elastic constants based on using cholesteric-nematic transition [4–6]. This technique is suitable for induced cholesterics with a wide range of chiral component concentrations of both mesogenic and non-mesogenic nature.

According to the mathematical model developed in [7,8], the threshold fields of forward E_{cn} and reverse E_{nc} cholesteric–nematic transitions can be found as:

$$Ecn = 2\sqrt{2}\left[\left[\frac{\pi}{Po}\right]^2\left(\frac{K_{22}}{\varepsilon_o\Delta\varepsilon}\right)+\frac{Fsn-Fsc}{d\varepsilon_o\Delta\varepsilon}\right]^{1/2}$$

$$Enc = \left[\left(\frac{\pi}{P_o}\right)^2\frac{(4K_{22}-K_{33}\frac{P_o}{d})^2}{\varepsilon_o\Delta\varepsilon K_{33}}+\frac{4Fsn}{d\varepsilon_o\Delta\varepsilon}\right]^{1/2}$$

,

where P_o is undistorted pitch of cholesteric helix; d is thickness of the LC layer; $\Delta\varepsilon$ is anisotropy of the dielectric permittivity; K_{22}, K_{33} are the Frank elastic constants; F_{sc}, F_{sn} are the surface energy densities of the corresponding states of LC.

These expressions enable us to take into account the influence of surface on the threshold fields through surface energy densities in the corresponding states.

Determining of elastic constants is carried out as follows:

1) *Determining of the Induced Helix Pitch*

In the CNMs with concentrations of optically active dopants (OAD) below 5% the pitch P_o can be determined using Grandjean–Cano steps in a wedge-shaped liquid crystal sample [9]. The measurement accuracy strongly depends on the quality of obtained disclinations. The measurement error typically does not exceed 3%.

Values of induced pitch in mixtures with OAD concentrations higher than 5% were determined from the selective reflection spectra in visible and near infrared regions. Given an extremely wide range of values of the induced helix pitch in mixtures with different concentrations of OAD, it was impossible to apply a single measurement technique as the measurement range was beyond the ability of any separate technique. Experiments were conducted in the range of temperatures 273–333 K.

2) *Measurements of Dielectric Anisotropy*

(i) For the mixtures with OAD less than 5% the dielectric anisotropy was determined according to the method described in [5].
(ii) LC materials possess a relatively small magnetic anisotropy; therefore, at considerable concentrations of cholesteryl oleat very large magnetic fields are required for unwinding of the LC helix. To overcome this problem, we used electric field in order to align the LC molecules and measured the capacitance of samples for the mixtures with OAD concentrations greater than 5%.

3) *Investigations of the Optical Transmission During the Cholesteric–Nematic Transition*

Studies of the laser radiation transmission dependencies *versus* applied voltage for induced cholesteric liquid crystal samples have been carried out according to the method described in [10]. A typical dependence of the laser radiation transmission *versus* applied voltage is presented in Fig. 1.

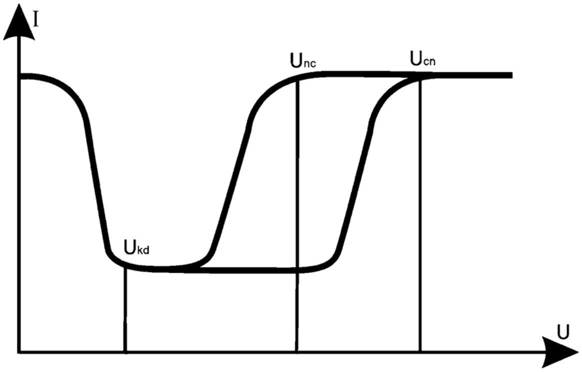

FIGURE 1 Typical dependence of laser radiation transmission *versus* applied voltage for induced cholesteric.

From the obtained dependencies of optical transmission, we determine the following threshold voltages and corresponding threshold electric fields:

1) U_{kd} is the threshold voltage of focal-conic deformation; $E_{kd} = U_{kd}/d$;
2) U_{cn} is the threshold voltage of forward transition; $E_{cn} = U_{cn}/d$;
3) U_{nc} is the threshold voltage of the reverse transition; $E_{nc} = U_{nc}/d$;

The experiments were carried out in the samples with the thickness of LC layer d of 3, 4, and 12 μm.

Elastic constants K_{22} and K_{33} were estimated independently by two different methods, on follows.

a) In the first approximation, one can assume that in the case of small changes in OAD concentration (within the limit of 3%) the values of elastic constants remain practically unchanged. This conclusion is confirmed by the results of X-ray studies of cholesteric structures [11].

The following expressions for the critical electric fields of the texture ($E_{c'c}$), forward (E_{cn}) and reverse (E_{nc}) transitions taking into account the surface interactions are the following:

$$Ec'c = 2\sqrt{2}\left[\frac{Fsc - Fsc'}{d\varepsilon_o\Delta\varepsilon}\right]^{1/2} \tag{1}$$

$$Ecn = 2\sqrt{2}\left[\left[\frac{\pi}{Po}\right]^2\left(\frac{K_{22}}{\varepsilon_o\Delta\varepsilon}\right) + \frac{Fsn - Fsc}{d\varepsilon_o\Delta\varepsilon}\right]^{1/2} \tag{2}$$

$$Enc = \left[\left(\frac{\pi}{P_o}\right)^2\frac{(4K_{22} - K_{33}\frac{P_o}{d})^2}{\varepsilon_o\Delta\varepsilon K_{33}} + \frac{4Fsn}{d\varepsilon_o\Delta\varepsilon}\right]^{1/2}, \tag{3}$$

where $F_{sc'}$, F_{sc}, F_{sn} are the densities of surface free energy in planar cholesteric, confocal, and nematic states. It should be noted that for the planar boundary conditions $F_{sc'} = 0$; for homeotropic, $F_{sn} = 0$. When developing the technique, it was assumed that the concentration dependencies of the threshold voltages of the cholesteric–nematic transition are linear. For convenience, we reduce expression (2) to the form

$$\frac{U^2cn}{d} = \frac{8\pi^2K_{22}}{\varepsilon_o\Delta\varepsilon}\cdot\frac{d}{P_o^2} + \frac{8(Fsn + Fsc)}{\varepsilon_o\Delta\varepsilon} \tag{4}$$

As one can see, expression (4) describes a straight line $U_{cn}^2 = f(d/P_o^2)$, the slope of which depends on K_{22} and $\Delta\varepsilon$, and the zero-order term enables us to find the value of $F_{sn} - F_{sc}$.

Using expressions (1) and (3) and the results of experimental measurements of the threshold voltages, induced helix pitch, and dielectric anisotropy within the given interval of temperatures, it is possible to define temperature dependencies of elastic constants K_{22} and K_{33}, and also to estimate the influence of surface conditions on the electro-optical properties of the cholesteric–nematic transition.

However, further experimental studies and analysis of the described theoretical approach demonstrated low accuracy of the measurements obtained by the linear approximation, in particular for K_{33}.

As an alternative method we used the following approximation:

1) To determine K_{22} from the results of experimental studies of the critical fields, a hyperbolic approximation was used:

$$Ecn = \left[8\frac{a_o}{P_o + a_1}\right]^{1/2},$$

where $a_o = \pi^2 K_{22}/\varepsilon_o \Delta\varepsilon,\ a_1 = Fsn - Fsc/\varepsilon_o \Delta\varepsilon \cdot d;$

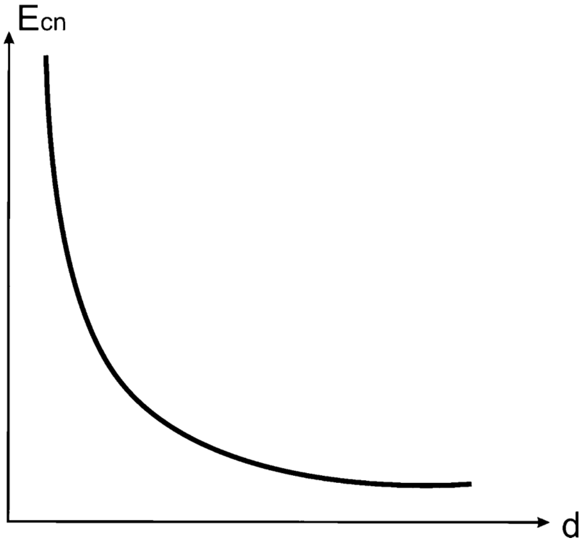

FIGURE 2 Hyperbolic dependence of E_{cn} *versus* d.

2) To determine K_{33}, we used the following parabolic approximation:

$$Enc = \left[\frac{a_1}{P_o^2} - \frac{a}{P_o + a_o}\right]^{1/2},$$

where $a = 8\pi^2 K_{22}/d\varepsilon_o\Delta\varepsilon$, $a_1 = 16\pi^2 K_{22}^2/K_{33}\varepsilon_o\Delta\varepsilon$, $a_o = K_{33}\pi^2 + 4Fsn\cdot d/d^2\varepsilon_o\Delta\varepsilon$;

3) As a result of the approximation, we obtained dependencies $E_{cn} = f(d)$ in the form of $Ecn = \sqrt{\frac{P_1}{d} + P_2}$ (Fig. 2), which enabled us to find the two parameters P_1 and P_2. By means of a data processing software (Origin 7), we determined numerically parameters P_1 and P_2 of the hyperbola, substituted these values in the (2) and obtained $P_1 = 8(Fsn - Fsc)/\varepsilon_o\cdot\Delta\varepsilon$ and $P_2 = 8\pi^2 K_{22}/P_o^2\cdot\varepsilon o\cdot\Delta\varepsilon$. As a result, we obtain two equations with two unknown ($Fsn - Fsc$ and K_{22}), as ε_o, $\Delta\varepsilon$, ${P_o}^2$ are known values.

We carried out parabolic approximation of formula (3), as a result the parabolic dependence $E_{cn}^2 = f(1/d)$ in the form of $E_{nc}^2 = A + B/d + C/d^2$ (Fig. 3). Similar to the previous case, we determine the numerical parameters A, B, and C of the line, and substitute them in approximated formula (3), where $C = \pi^2 K_{22}/\varepsilon_o\cdot\Delta\varepsilon, B = 4F_{sn}/\varepsilon_o\cdot\Delta\varepsilon - 8K_{22}\pi^2/\varepsilon_o\Delta\varepsilon P_o$, $A = 16\pi^2 K_{22}^2/\varepsilon_o\Delta\varepsilon K_{22}P_o^2$.

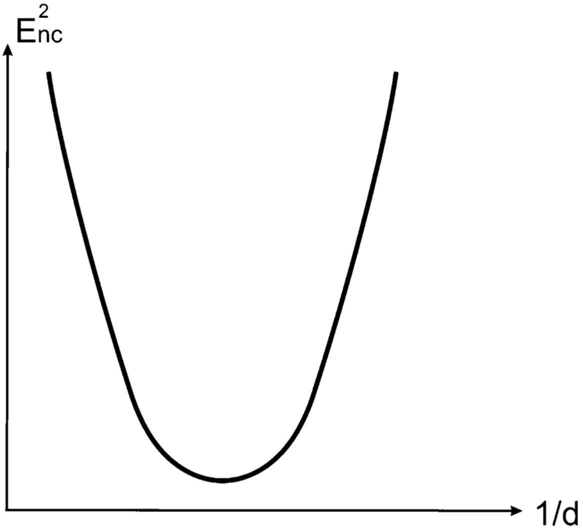

FIGURE 3 Parabolic dependence of E_{cn}^2 *versus* 1/d.

TABLE 1 Dielectric Anisotropy for Different Cholesteryl Oleat Concentrations

Composition (weight.%)		$\Delta\varepsilon$ at 333 K
SZK-654	Cholesteryl oleat	
98	2	10.5
96.8	3.2	10.4
95.9	4.1	10.3
92.5	7.5	9.96
89.8	10.2	9.67
86.4	13.6	9.3
82.5	17.5	8.9
75	25	8.08
63.4	36.6	6.8
60	40	6.4

EXPERIMENTAL RESULTS

The values of dielectric anisotropy for different cholesteryl oleat concentrations at the temperature 333 K are shown in Table 1.

The dependence of 1/P (the reverse value to the helical pitch) on content of the cholesteryl oleat dopant in the range of temperatures 273–333 K is presented in Fig. 4.

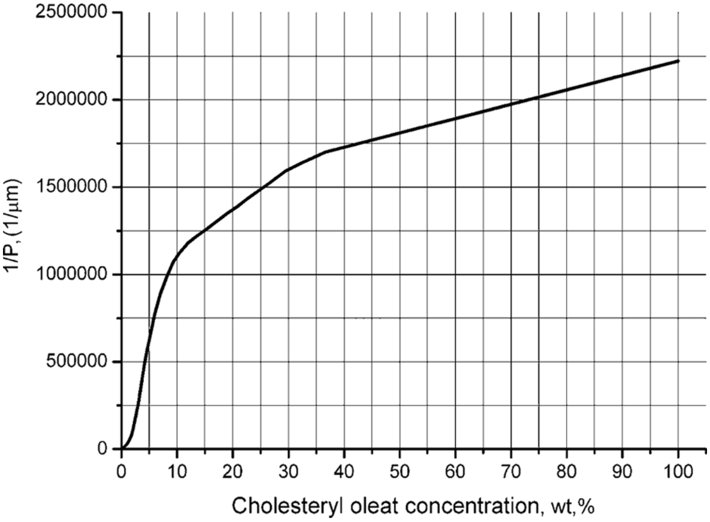

FIGURE 4 Dependence of 1/P on the concentration of cholesteryl oleat.

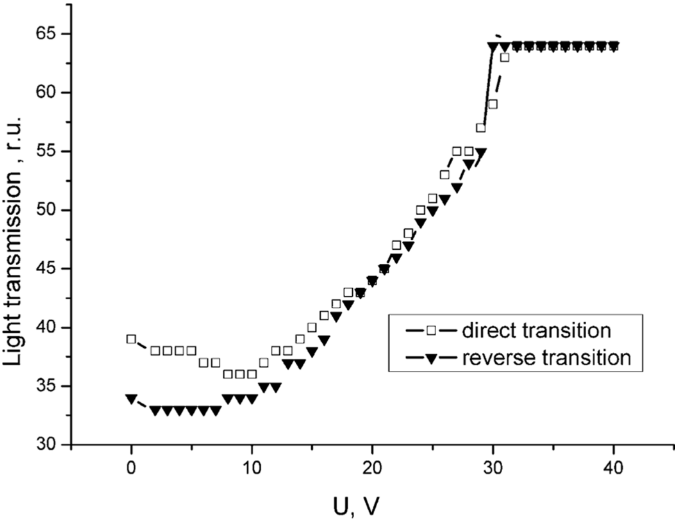

FIGURE 5 Dependence of light transmission on the applied voltage for the LC-654 + 37% cholesteryl oleat CNM (the thickness of LC layer IS 3.6 μm).

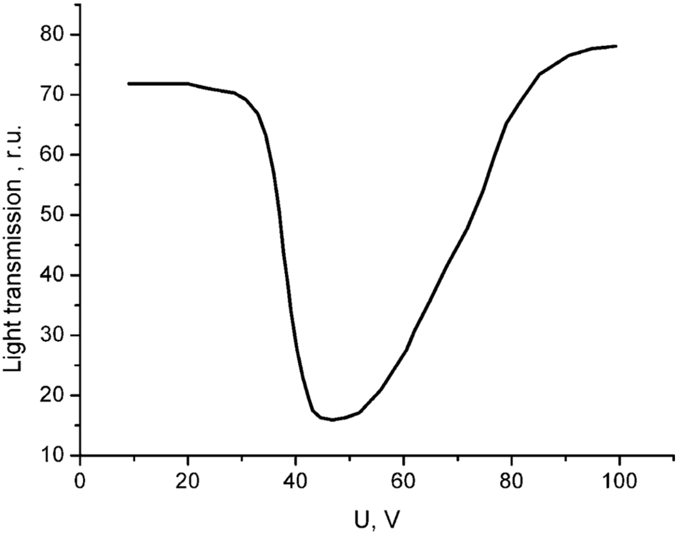

FIGURE 6 Dependence of light transmission on the applied voltage for the LC-654 + 37% cholesteryl oleat CNM (the thickness of liquid crystal layer IS 12 μm).

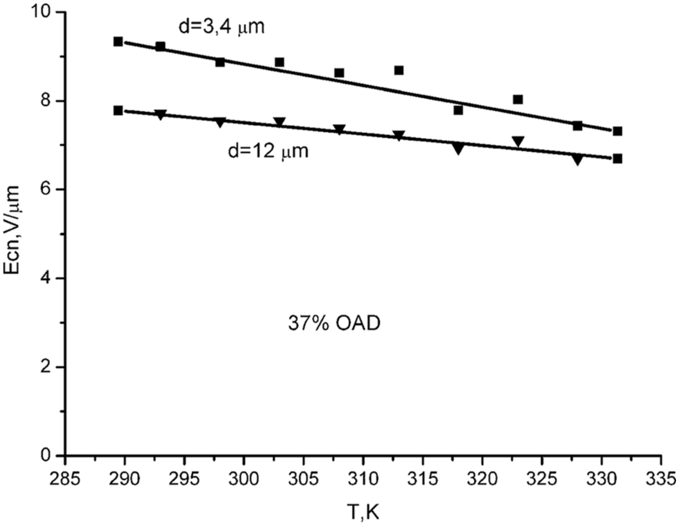

FIGURE 7 Temperature dependencies of the critical field of forward cholesteric–nematic transition of the LC-654 + 37% cholesteryl oleat mixture (the thickness of liquid crystal layer IS 12 and 3.4 μm).

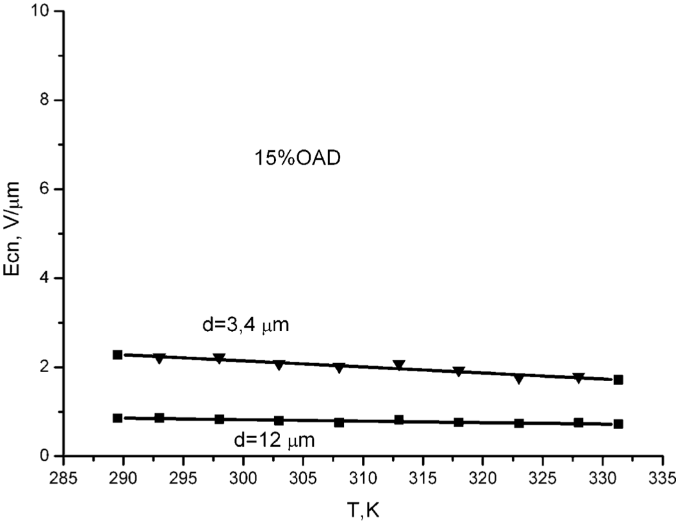

FIGURE 8 Temperature dependencies of the critical field of forward cholesteric–nematic transition of the LC-654 + 15% cholesteryl oleat oleat mixture (the thickness of liquid crystal layer IS 12 and 3.4 μm).

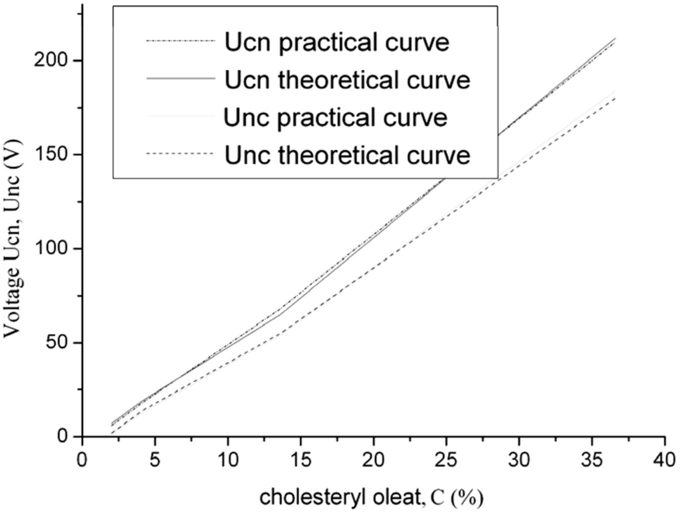

FIGURE 9 Dependence of the theoretical (dotted line) and experimental (continuous line) voltage Ucn and Unc on dopant concentration C.

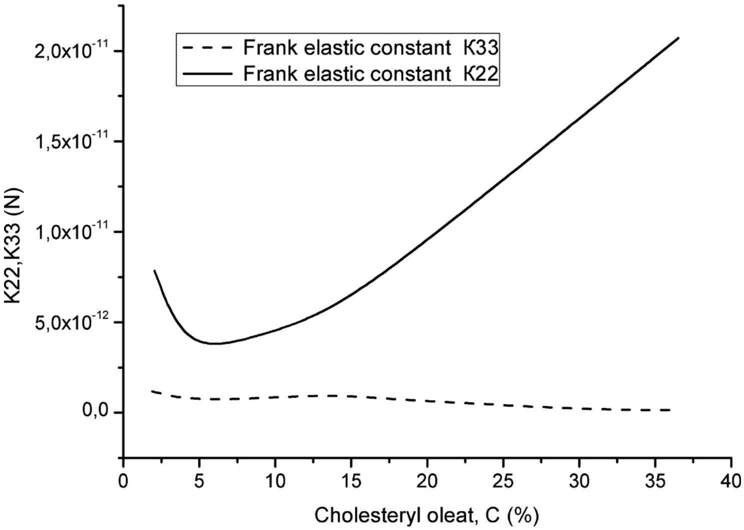

FIGURE 10 Dependence of the Frank elastic constants K_{22}, K_{33} on OAD concentration C.

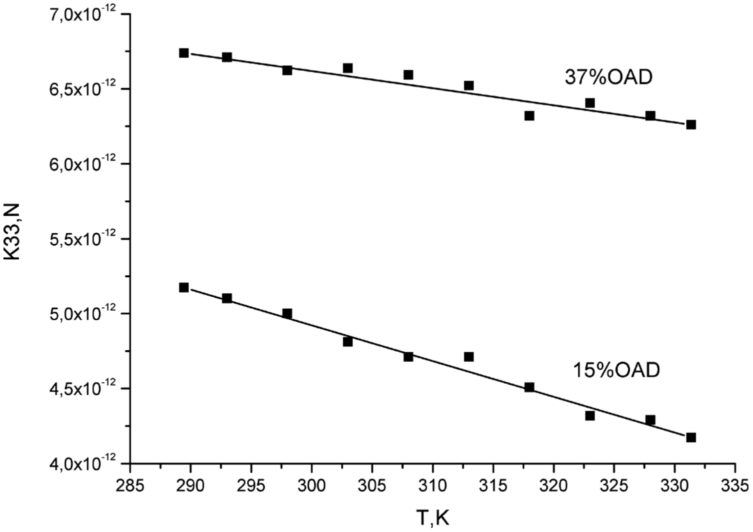

FIGURE 11 Temperature dependencies of the elastic constants K_{33} for the mixtures of LC-654 + 37% cholesteryl oleat, LC-654 + 15% cholesteryl oleat.

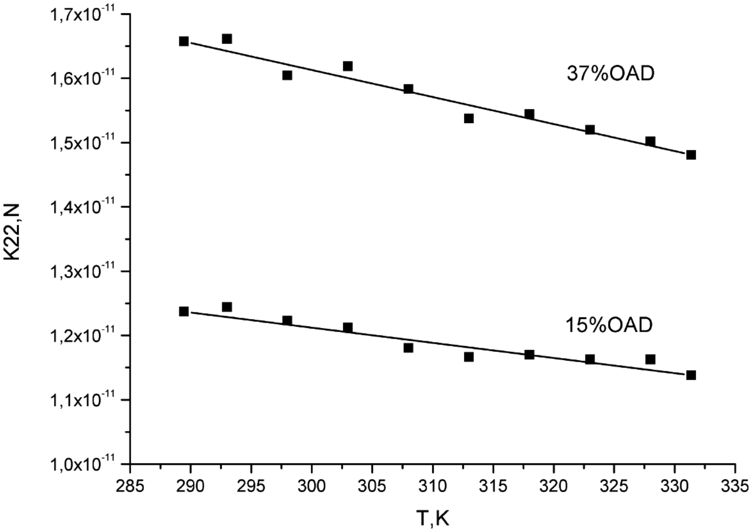

FIGURE 12 Temperature dependencies of the elastic constant K_{22} for the mixtures of LC-654 + 37% cholesteryl oleat, LC-654 + 15% cholesteryl oleat.

The obtained results have shown that the increase of dopant concentration leads to the decrease of the helical pitch. The helix pitch was measured in the range 9.5–0.45 μm for the selected range of the cholesteryl oleat concentrations; the dependence of 1/P being of a non-linear character.

The dependencies of optical transmission on the applied voltage for the CNMs with different cholesteryl oleat concentrations are shown in Figs. 5 and 6.

Analysis of the obtained results showed that increase of dopant concentration leads to the increase of threshold voltages. However increase of the LC layer thickness for a mixture with a fixed content of cholesteryl oleat causes the decrease of the critical electric fields, which could be explained by the decrease of influence of near-surface effects.

The temperature dependencies of the threshold electric field of the forward cholesteric–nematic transition for mixtures with different cholesteryl oleat concentrations (15 and 37%) are presented in Figs. 7 and 8. The experimental results have shown, that the temperature increase resulted in insignificant decrease of the threshold field, which is caused by the decrease of elastic constants.

The dependencies of the cholesteric–nematic transition voltage on the dopant concentration were investigated. Figure 9 shows that the increasing of OAD concentration results in increasing of critical voltages values of effect of cholesteric-nematic transition; moreover, the dependence has practically linear character. The obtained experimental results are in good agreement with theory [7]. The concentration dependences of the elastic constants K_{22}, K_{33} for different cholesteryl oleat concentrations (15 and 37%) are presented in Fig. 10. The nonlinear type of the dependence is caused by the change of character of intermolecular interaction of molecules of nematic matrix and cholesteric dopant in the range of the concentrations 4–12%. Elastic constants were determined in the temperature range 288–328 K (Figs. 11 and 12).

Also we carried out the calculations of the elastic constants K_{11} according to theoretical approach suggested by Leslie [12]

$$E_{c'c} = \frac{\pi}{P_o}\left[\frac{K_{11}\left(\frac{P_o}{d}\right)^2 + 4K_{33}}{\varepsilon_o \Delta\varepsilon}\right]^{1/2}.$$

The results of this study are presented in Table 2 (for the room temperature).

TABLE 2 Frank Elastic Constants K_{11}

Composition (wt.%) of *cholesteryl oleat* in SLC-654	2	3.2	4.1	7.5	10.2	13.6	17.5	25	36.6	40
Frank elastic constant K_{11}, N	$1.6 \cdot 10^{-10}$	$1.5 \cdot 10^{-9}$	$2.5 \cdot 10^{-9}$	$3.1 \cdot 10^{-9}$	$3.7 \cdot 10^{-9}$	$4.4 \cdot 10^{-9}$	$7.5 \cdot 10^{-9}$	$1.45 \cdot 10^{-9}$	$2.5 \cdot 10^{-8}$	$2.79 \cdot 10^{-9}$

CONCLUSIONS

The method of determination of the elastic constants K_{22} and K_{33} was developed. The method is based on the mathematical model, which calculates the expressions for threshold fields of direct and reverse cholesteric–nematic transition. Also this mathematical model takes into account the influence of surface on the threshold fields. According to this mathematical model the threshold fields are determined through the spiral pitch, dielectric anisotropy, critical fields of focal-conical deformation, voltage of the direct and reverse cholesteric–nematic transition. The hyperbolical and parabolic approximations of experimental dependencies were used, that provide the possibility to increase the accuracy of calculations. Particularly, the values of the constant K_{11} have been calculated.

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