

ELECTRO-OPTIC CHARACTERISTICS OF LIQUID CRYSTALLINE MIXTURE H-37 DOPED BY FERROELECTRIC PARTICLES

T.D. IBRAGIMOV^a, A.R. IMAMALIYEV^a, G.M. BAYRAMOV^{a,b}

Institute of Physics of Azerbaijan National Academy of Sciences^a,

131 H.Javid Avenue, Baku, AZ1143, Azerbaijan, E-mail:tdibragimov@mail.ru

Baku State University^b. 23 Z.Khalilov Street, AZ1148. Baku, Azerbaijan

Influence of barium titanate particles on electro-optic properties of the nematic liquid crystalline (LC) mixture H-37 consisting of 4-methoxybenzylidene-4'-butylaniline and 4-ethoxybenzylidene-4'-butylaniline was investigated.

It was shown that the occurrence of barium titanate particles into H-37 decreases clearing temperature, increases the threshold of the Fredericksz effect and decreases the voltage of the electrohydrodynamic instability formation. A rise time increases and a decay time decreases in comparison with the pure H-37. First of all, experimental results are explained by appearance of local electric fields near the polarized ferroelectric particles at application of external electric field and also a change of viscosity and elastic properties of LC, existence of the additional obstacles (particles) by ions.

Keywords: liquid crystal, Fredericksz effect, electrohydrodynamic instability, small particles, barium titanate.

PACS: 42.70.Df; 47.20.Cn; 47.32.Cd; 61.30.Gd.

1. INTRODUCTION

One of directions of modern technology and physics of liquid crystals (LC) is development of hybrid systems, in particular, consisting of small particles embedded in a LC matrix. Even through at sufficient large particles (an order of wavelength of incident radiation) there is an optical effect of transmission of the system in a narrow spectral region, a maximum of which is shifted by action of electric field [1-5]. Besides, particles influence on electro-optical effects in LC, causing changes of their parameters [6-7].

It has been shown in the work [8] that there is no disturbance of the director of LC molecules if anchoring parameter of LC molecules with the particle surface is less than 1 and at their small concentration. This parameter depends on the particle sizes, elastic properties of LC, and also anchoring energy. At a certain combination of the specified parameters, the colloid behaves as a pure LC but with changed characteristics. Particularly, there is an increase of the order parameter of LC, reduction of clearing temperature [9], and also a decrease of threshold voltages.

There can appear additional effects if a particle substance is ferromagnetic or ferroelectric material. It was shown in one of the first works [10] that an additive of ferromagnetic particles in a LC matrix at small concentration leads to an increase of LC sensitivity to magnetic fields.

Authors of the work [11] obtained stable colloids based on of iron oxide particles in a liquid crystal 5CB and showed that their electro-optic properties slightly differed from the pure LC but possessed a property of a magnetic liquid. Recent years similar researches have started to be carry out with a system of ferroelectric particles in a LC.

It has been shown that at additive of ferroelectric particles increases dielectric response of LC and changes its conductivity [12-13], and also produces the photorefractive effect [14]. The memory effect in an isotropic phase of the liquid crystal 5CB doped by barium titanate particles was also observed [15].

One of the most used electro-optic effects in liquid crystal (LC) with negative dielectric anisotropy is electrohydrodynamic instability (EHDI). It is electric-induced phenomenon that is caused by the flow of a liquid crystal. Due to the flow distortion of the director alignment, the instability is usually accompanied by characteristic optical pattern. Among the instabilities in LC the most known are the Carr-Helfrich instability which is arises in a homogeneously oriented LC layer in a sandwich cell between transparent electrodes [16]. It is caused by a low-frequency electric field and occurs in the form of elongated vortices with their axis perpendicular to the original director alignment. The vortices cause a distortion of the director orientation, which is observed optically as a one-dimensional periodic pattern. They are called by Williams' domains.

In the present work, we have studied influence of embedded ferroelectric barium titanate particles on electro-optic characteristics of liquid crystalline mixture H-37 with negative dielectric anisotropy.

2. EXPERIMENTAL

We used liquid crystalline mixture consisting of 4-methoxybenzylidene-4'-butylaniline (MBBA) and 4-ethoxybenzylidene-4'-butylaniline (EBBA) with molar ratio of 1:1 (H-37) as a matrix. Selection of the present mixture is also based on following facts: a dielectric anisotropy is negative and conductive along the director is more than one perpendicular to the director for this LC. It was the opportunity for the EHDI study in nematic LC since the occurrence of field effects was excluded and it was only observed in planar sample of LC with negative dielectric anisotropy [8]. The monodisperse fraction of barium titanate particles with the average size of 600 nm was mixed with oleic acid and heptane in the ratio of 1:2:10 and ultrasonically dispersed for 1 hour. Then, the obtained mixture was added in the liquid crystal and kept at temperature 60 °C for 5 days till complete evaporation of heptane. The evaporation control of heptane was by weighing on analytic balance. The final composition was ultrasonically mixed. As a result, the colloid with weigh

percent 1% of particles was obtained. The image of the colloid under polarization microscope is represented in Fig.1.

The experiments were carried out in the electro-optic cell. The latter had a sandwich structure and consisted of two plane-parallel glass plates whose inner surfaces were coated with thin transparent and conductive layer ITO (Indium-Tin-Oxide). It was made from two glass substrates whose inner surfaces were coated with conducting indium-tin-oxide (ITO) layers. The cells' thickness was fixed with calibrated 17 μm polymer spacers. Either the colloid or the pure LC was filled into the cell by capillary action at isotropic state.

A setup for measurements of electro-optical parameters was assembled on the base of the polarization microscope of firm Carl Zeiss Jena. Impulses of the special form applied on the cell by the functional generator G6-28. A light passing through the cell fell on the photo diode and was registered by digital storage oscilloscope 6022BE of the firm HANTEK. Switching times and contrast were defined at application of unipolar rectangular impulses while threshold voltage was recorded using unipolar triangular impulses in quasi-static regime. Besides, value of threshold voltage was supervised under the polarization microscope. Frequency dependence of threshold voltage was registered at application of sinusoidal voltage. All measurements were carried out at temperature 21 $^{\circ}\text{C}$.

3. RESULTS

Results of measurements have shown that the used concentration of the additive of barium titanate particles inside the liquid crystal H-37 shifts the clearing point from 61.2 $^{\circ}\text{C}$ to 60.1 $^{\circ}\text{C}$.

Threshold voltage of Fredericksz effect increases from 2.8 V to up 3.1 V at addition of particles and remains practically constant up to the frequency of 700 kHz of the applied electric field then it drastically increases up to 3.4 V and 4.2 V near the frequency of 1 MHz for the pure LC and the colloid, accordingly (Fig. 1).

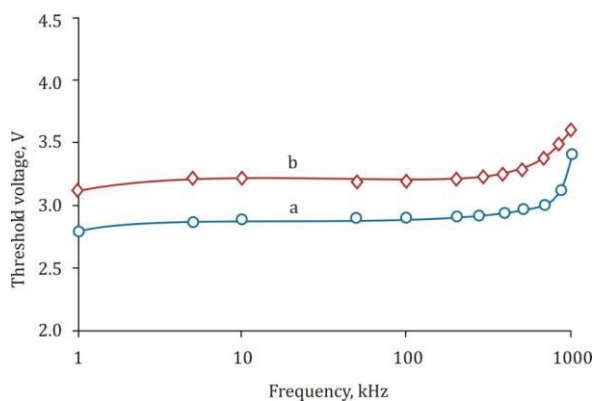


Fig.1. Frequency dependence of the threshold voltage of the Fredericksz effect: (a) pure H-37, (b) H-37 + BaTiO₃.

The threshold voltage of the Williams domain formation of the colloid equals to 3.7 V at application of quasi-static electric field while these domains begin to

form inside the cell with the pure LC at 6.3 V. Frequency dependence of threshold voltage of both pure H 37 and with an addition of particles is shown in Fig. 2.

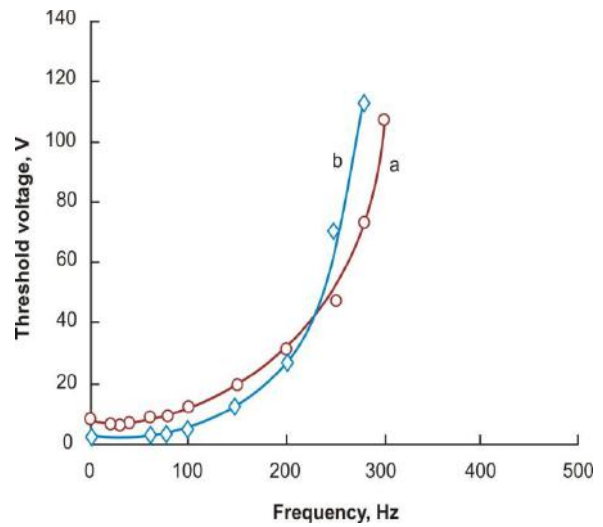


Fig.2. Frequency dependence of the threshold voltage of the Fredericksz effect: (a) pure H-37, (b) H-37 + BaTiO₃.

Indicated dependence is similar for both samples: with frequency increasing the threshold voltage increases and it aspires to infinity at some frequency, indicating on disappearance of the EHDI effect. The occurrence of barium titanate particles in LC reduces the threshold voltage of the EHDI formation in a quasi-static field and at low frequencies while it increases this threshold at high frequencies. At this case, we did not observe the disappearance of the instability in the colloid.

Time characteristics of the EHDI effect are resulted in Figs. 3 and 4.

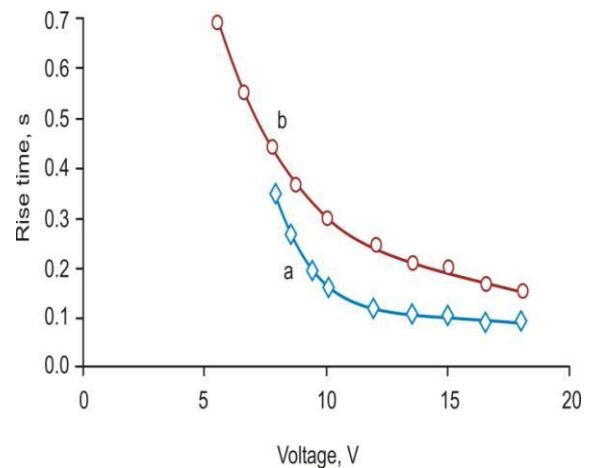


Fig.3. Dependence of rise time on quasi-static field voltage : (a) pure H-37, (b) H-37 + BaTiO₃.

Apparently, a rise time decreases with increasing of the applied voltage. An addition of particles into H-37 increases a rise time at all voltages. A decay time of the colloid less than for the pure LC at all applied voltages. At this case, a minimum is observed in corresponding dependence of the colloid at voltage 10 V. Observation under microscope shows chaotic motion of particles at this voltage.

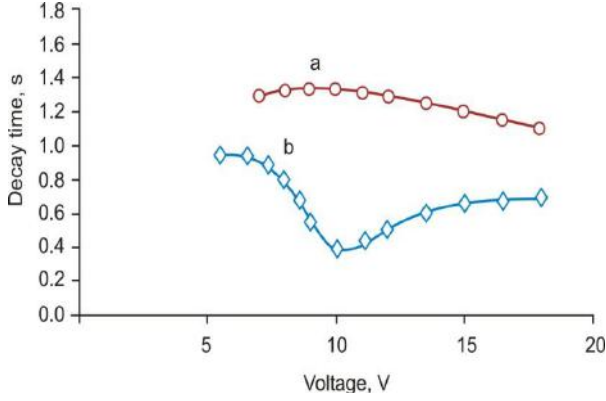


Fig.4. Dependence of decay time on quasi-static field voltage : (a) pure H-37, (b) H-37 + BaTiO₃.

Apparently, a rise time decreases with increasing of the applied voltage. An addition of particles into H-37 increases a rise time at all voltages. A decay time of the colloid less than for the pure LC at all applied voltages. At this case, a minimum is observed in corresponding dependence of the colloid at voltage 10 V. Observation under microscope shows chaotic motion of particles at this voltage.

4. DISCUSSION

According to [8], particles do not disturb the director of a LC, if the anchoring parameter $\zeta = WR/K_{11}$ is much smaller than 1, where W – anchoring energy of LC molecules with particle surfaces, $2R$ is particle size, K_{11} is the LC splay elastic constant. The values of anchoring energy is within 10^{-4} - 10^{-6} J/m², elastic constant of H-37 equals to $7.1 \cdot 10^{-12}$ N, and $2R$ has the size of 600 nm. Using oleic acid we reduce anchoring energy and simultaneously stabilize the colloid.

Besides, taking into account utilized concentration of particles, particle sizes, and particle density one can calculate that average distance between particles equal to 7.5 μ m which is about 10 times more than the particle sizes.

Thus, the overall disturbance of the director field by particles appears negligibly small. Hence, the obtained colloid can be considered as a homogeneous medium and it should behave as pure LC but with the modified parameters.

According to the calculations resulted in [17], at the spherical form and small concentration of particles, clearing temperature T_c of a colloid is defined by the formula

$$T_c = (1-f_v) T_{cp},$$

where f_v is volume concentration of particles, T_{cp} is clearing temperature of a pure LC.

Volume concentration of barium titanate particles equals to 0.002 but the total volume concentration of the filler inclusive of oleic acid amounts to 0.024. One can see, the calculations fairly well agree with the experimental value of clearing temperature.

At the sizes of particles greater than 100 nm with a lack of external electric field, the ferroelectric particles have a polydomain state [18], that is, there are the domains which polarization are oriented to various directions and fields of which compensate each other. Under the influence of external electric field inside the colloid, the dipole moments of domains are gradually established in the field direction. Herewith, they create around themselves the local electric field with a maximal value defined by the expression:

$$E = R^3 P_s / 3\epsilon\epsilon_0 r^3.$$

here, $2R$ is particle size, P is spontaneous polarization, ϵ is dielectric permittivity of a LC, ϵ_0 is the electric constant, and r is distance from the center of a particle to the given point of the field. Considering the numerical values of the parameters ($R = 300$ nm, $P_s = 0.26$ C/m², $\epsilon \approx 10$, $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m) one can show, in particular, that the local field has of an order of 10^{10} V/m at the distance of 300 nm from a particle surface, which dramatically decreases in inverse proportion to a cube of distance from the particle center. This field orientates dipoles of LC molecules near the particles along electric-field lines. With further increase in the field intensity, the dipoles of particles together with the nearest LC molecules turn under the influence of the field in the aggregate.

Threshold voltage of the Fredericksz effect for a pure LC, and also a low-concentrated colloid is defined by expression [19]:

$$U_{th} = \pi (K_{33}/\epsilon_0 \Delta\epsilon)^{1/2},$$

where K_{33} is the bend elastic constant, ϵ_0 is the electric constant, $\Delta\epsilon$ is the dielectric anisotropy.

The larger value of threshold voltage of the colloid in comparison with the pure LC is connected with two competitive factors: presence of particles increasing the order parameter [18] and oleic molecules decreasing this parameter which affects on the dielectric anisotropy of the colloid. Most likely, the oleic acid molecules have more influence on the LC than particles.

Hence, the order parameter and, correspondingly, the dielectric anisotropy decrease. As a result, the threshold voltage increases.

There is a dispersion of $\epsilon_{||}$ at 750 kHz because of the LC molecules have no time to turn about a short axis at fast changes of the direction of the applied field while ϵ_{\perp} does not almost vary as it corresponds to turn of LC molecules around the long axis. Consequently, a dielectric anisotropy decreases and, accordingly, a threshold voltage increases.

The physical mechanism of the instabilities could be described as follows. A homogeneously oriented nematic LC is stabilized by the elastic torque due to anchoring of LC molecules with a substrate surface. Dielectric torque because of both external and space charge fields is stabilizing for LC with negative dielectric anisotropy. Owing to an electric field, the arising torque also is stabilizing. The ions are charge carriers in the nematic phase, whose mobility along long molecular axis is greater than the mobility perpendicular to this direction.

As a result, the electroconductivity is greater in one direction than in another. Therefore, nematic LC usually has positive anisotropy of electroconductivity. The space charge can be formed owing to this anisotropy because of ion division.

The applied field acts on charges, causing occurrence of the substance flow in reciprocal directions. It creates the unstable torque induced by the electroconductivity and acting on molecules. The EHDI effect arises if this torque exceeds all other torques. At low frequencies of an applied field, the instability mode is characterized by that a space charge oscillates with a field frequency. At the same time, so far as the threshold of the Williams domain occurrence is low, a reaction time of the director is sufficiently great. Thus, the threshold voltage sharply increases at approaching to the critical frequency f_c which is connected with a dielectric relaxation τ_c by the relationship [20]:

$$f_c = (\zeta^2 - 1)^{1/2} / \tau_c$$

where $\zeta^2 = \varepsilon_{II}^2 \eta_B (\varepsilon_{\perp} / \varepsilon_{II} - \sigma_{\perp} / \sigma_{II}) / \Delta \varepsilon \varepsilon_{\perp} \eta$ is called by Helfrich parameter; ε_{II} and ε_{\perp} are components of dielectric permittivity, $\Delta \varepsilon$ is dielectric anisotropy; η is the effective viscosity; σ_{II} and σ_{\perp} are electroconductivities along and normal to the director, respectively.

The threshold voltage for static and low frequency field in the case of planar configuration of nematic LC with negative dielectric anisotropy is defined by the formula:

$$U_{th} = -4\pi^3 \varepsilon_{II} K_{33} / \Delta \varepsilon \varepsilon_{\perp} (\zeta^2 - 1),$$

where η_B is the corresponding viscosity for bend deformation. A rise time of the instability is defined by the expression:

$$t_{rise} = \beta \eta_B d^2 / (U^2 - U_{th}^2),$$

while a decay time has the form:

$$t_{decay} = \alpha \eta_B d^2 / \pi^2 K_{33},$$

where α and β are the coefficients depending on LC parameters; d is the cell thickness; U is the voltage of applied static field.

Though the ionic current follows an external field, a separation process of a space charge phase lags on the phase from a field with frequency increasing. It leads to reduction of force influence on a space charge from an external field. The torque corresponding to conductivity,

decreases and it is required to raise an external voltage for instability achievement that is confirmed by the experiment (Fig. 5).

Inclusion of particles in LC feebly alters dielectric permeability and conductivity properties of LC in a static field. Probably, a change in the threshold voltage is connected with other reasons. Barium titanate particles in LC induce development of instability at lower threshold because they are the turbulence centers in LC. At the same time, with increasing of the external field frequency nonconducting particles prevent to a movement of ions and it is required greater voltage to maintain the instability. In connection with it, there is a sharper increase of threshold voltage with a frequency change.

According to the above mentioned expressions, a rise time decreases with voltage increasing that is proved by the experiment. In this case, a presence of particles increases a rise time in comparison with the pure LC. First of all, it is connected with an increase in effective viscosity and a reduction of elastic properties of LC and also with overcoming the additional obstacles (particles) by ions. Furthermore, at application of an external electric field, dipoles of LC molecules near the polarized ferroelectric particles are orientated along electric-field lines, namely, normal to the substrate surface, enhancing the initial homeotropic configuration of the LC molecules. Thereat, an additional torque is formed, which increases a rise time and decreases a decay time in comparison with pure LC at the same voltages. At this case, a minimum in voltage dependence of decay time is connected with polarization of areas near the particles existing an addition torque and promoting chaotic motion of particles.

CONCLUSIONS

It was shown that the occurrence of barium titanate particles in H-37 decreases clearing temperature increases the threshold of the Fredericksz effect, decreases the voltage of the EHDI formation. A rise time increases and a decay time decreases in comparison with the pure H-37. First of all, experimental results are explained by appearance of local electric fields near the polarized ferroelectric particles at application of external electric field and also a change of effective viscosity and elastic properties of LC, existence of the additional obstacles (particles) by ions.

ACKNOWLEDGMENT

This work was supported of the Science and Technology Center in Ukraine (grant no. 5821).

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Received: 29.01.2015