Instability mechanism in the nematic and isotropic phases of liquid crystals with positive dielectric anisotropy

M. I. Barnik, L. M. Blinov, S. A. Pikin, and A. N. Trufanov

Scientific Research Institute of Organic Intermediates and Dyes
(Submitted July 22, 1976)
Zh. Eksp. Teor. Fiz. 72, 756–761 (February 1977)

An investigation has been made of the frequency characteristics of the threshold of electrohydrodynamic instability in the nematic and isotropic phases of liquid crystals as functions of the electrical conductivity, the viscosity, and the dielectric properties of the medium. It is shown that the mechanisms are identical in the onset of instability in homeotropically oriented nematic liquid crystals with positive dielectric anisotropy and in isotropic liquids (and also in the so-called "dielectric" regime when the dielectric anisotropy is negative). A theoretical calculation of electroconvective phenomena in an isotropic liquid leads to an explanation of the observed regularities.

PACS numbers: 77.90.+k

1. INTRODUCTION

It is well known[1] that in planarly oriented nematic liquid crystals (NLC) with negative dielectric anisotropy ($\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp < 0$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the dielectric constants for directions parallel and parallel to the NLC director), electrohydrodynamic (EHD) instability occurs at frequencies below the critical ($\omega_c = 2\pi f_0 \approx 4\pi\sigma/\varepsilon$, where σ is the electrical conductivity) in the form of Williams domains, and at frequencies $\omega \gg \omega_c$ in the form of "chevrons" with a characteristic frequency dependence of the threshold field $E_{th} \sim \omega^{1/2}$.[2,3]

Another characteristic case, in which the beginning of EHD instability is not preceded by a stage of director reorientation, is a homeotropically oriented NLC with $\varepsilon_a > 0$. Within the framework of a theory based on consideration of the anisotropy of the electrical properties of the material, this case is considered to be electrohydrodynamically stable.[4] But experimentally, EHD instability is observed in this case also, in the form of rather complicated domain patterns.[5,6]

In the present paper, an investigation is made of the connection between the threshold field for occurrence of instability in a homeotropically oriented NLC with $\varepsilon_a > 0$ and the physical parameters of the material (electrical conductivity, dielectric constants, viscosity), for the purpose of explaining the mechanism of this instability. In the solution of this problem it became necessary to investigate also EHD instability in the isotropic phase.

2. EXPERIMENTAL METHOD

The frequency dependence of the threshold voltage (U_{th}) for formation of domain patterns in the nematic phase was recorded by means of a polarizing microscope, and also by a photoelectric method, in cells of the usual type, of thickness 20 μm. Homeotropic orientation of the NLC was achieved by thorough cleaning of SnO_2 electrodes. The substance used in the experiments was MBBA (*p*-*n*-methoxybenzylidene-*p*′-butylaniline), mixed with tetrabutylammonium bromide to obtain electrical conductivities in the range $10^{-11} < \sigma_\parallel < 5 \cdot 10^{-9}$ ohm^{-1} cm^{-1} ($\sigma_\parallel$ is the electrical conductivity for the direction parallel to the NLC director) and with *p*′-cyanophenyl ester of *p*-*n*-heptylbenzoic acid (CEHBA) for variation of the value of ε_a over the range 0 to +3 (at 20 °C). The experimental investigations of $U_{th}(f)$ were made with a sinusoidal voltage (20 Hz < f < 10 kHz), although use was also made of pulses of rectangular shape (it was established that U_{th} is practically independent of the shape of the signal and determined by the effective value of the voltage).

The onset of instability in the isotropic phase was recorded on the basis of the beginning of circular motion of solid foreign particles. The accuracy of determination of U_{th} was ± 5% when domain patterns were recorded and ± 10% when motion of particles was observed.

3. EXPERIMENTAL RESULTS

Figure 1 shows the frequency dependence of the threshold voltage for EHD instability for NLC with various values of σ and ε_a. On the curves, two regions can be clearly distinguished: a plateau region at frequencies less than the critical, and a region of square-root dependence $U_{th} \sim f^{1/2}$ at frequencies $f > f_c$. The form of the domain patterns is completely different for these two

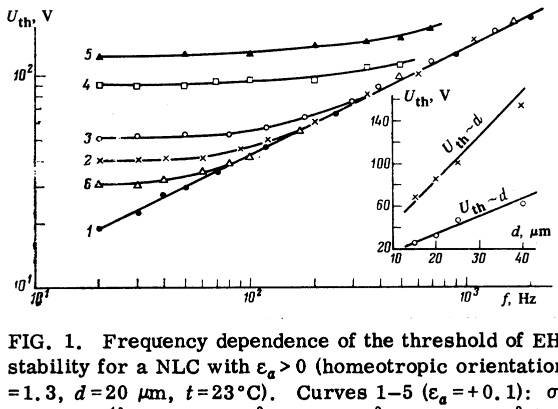

FIG. 1. Frequency dependence of the threshold of EHD instability for a NLC with $\varepsilon_a > 0$ (homeotropic orientation, $\sigma_\parallel/\sigma_\perp = 1.3$, $d = 20$ μm, $t = 23$ °C). Curves 1–5 ($\varepsilon_a = +0.1$): $\sigma_\parallel = 4 \cdot 10^{-11}$ (1), $7 \cdot 10^{-10}$ (2), $1.2 \cdot 10^{-9}$ (3), $3 \cdot 10^{-9}$ (4), $5.5 \cdot 10^{-9}$ (5) ohm^{-1} cm^{-1}; Curve 6, $\varepsilon_a = +3$, $\sigma_\parallel = 8 \cdot 10^{-10}$ ohm^{-1} cm^{-1}, Insert: dependence of the threshold of EHD instability on the thickness of the NLC layer ($\varepsilon_a = +0.1$, $\sigma_\parallel \approx 5 \cdot 10^{-10}$ ohm^{-1} cm^{-1}): o, $f = 20$ Hz ($f < f_c$); ×, $f = 400$ Kz ($f > f_c$).

 0038-5646/77/4502-0396$02.40

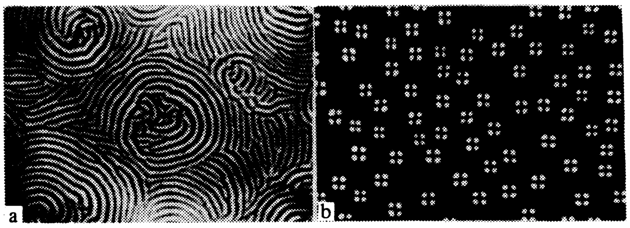

FIG. 2. Form of domain patterns of EHD instability in a NLC with $\varepsilon_a > 0$ (homeotropic orientation, $d = 20$ μm). a, domains of "fingerprint" type at frequencies $f < f_c$ ($\varepsilon_a = +0.1$, $\sigma_\parallel = 4 \cdot 10^{-10}$ ohm^{-1} cm^{-1}, $f = 30$ Hz); b, circular domains at frequencies $f > f_c$ ($\varepsilon_a = +0.1$, $\sigma_\parallel = 4 \cdot 10^{-11}$ ohm^{-1} cm^{-1}, $f = 100$ Hz). Dimensions of the photographs are 1000×700 μm (Fig. a) and 600×410 μm (Fig. b).

cases: when $f < f_c$, domains of the "fingerprint" type are observed (Fig. 2a); when $f > f_c$, domains in the form of Maltese crosses, called "circular" in Ref. [5] (Fig. 2b). In the latter case, the solid foreign particles complete their circular motion within the crosses of circular domains. At frequencies $f < f_c$ the particles execute translation motion along domain loops, but at nodes of the loops their motion has a circular character, just as at frequencies[1)] $f > f_c$.

We shall note the most important features of Fig. 1.

a) Just as in the case $\varepsilon_a < 0$ (the "dielectric" regime),[2,3] the instability has a field threshold: U_{th} is proportional to the thickness d of the cell (see insert in Fig. 1; the measurements were made on a wedge-shaped cell with electrodes in the form of narrow strips parallel to the vertex of the wedge). Here $U_{th} \sim d$ both at low frequencies ($f < f_c$) and at high ($f > f_c$).

b) The threshold voltage $U_{th}(f)$ at frequencies $f > f_c$ is practically independent of the dielectric anisotropy ε_a (Curve 6 was obtained at $\varepsilon_a = +3$, the remaining curves at $\varepsilon_a = +0.1$; that is, ε_a varies in the experiment by a factor 30; also in quantitative agreement with Curves 1–6 is the function $U_{th}(f)$ obtained on 4-p-hexyl-4′-cyanobiphenyl, with $\varepsilon_a = +10$). In the frequency range $f < f_c$, with $\sigma = \text{const}$, the voltage $U_{th}(f)$ decreases noticeably with increase of the mean value of the dielectric constant $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ (compare Curves 2 and 6).

c) With increase of the electrical conductivity, the low-frequency ($f < f_c$) instability threshold increases according to the law $U_{th} \sim \sigma^{1/2}$ (Curves 1–5), while the high-frequency ($f > f_c$) threshold is independent of σ. Over the whole range of frequencies, the threshold voltage $U_{th}(f)$ is independent of the anisotropy of the electrical conductivity, $\sigma_a = \sigma_\parallel - \sigma_\perp$ (the latter was determined by special experiments).

d) The high-frequency branch of the curves $U_{th} \sim f^{1/2}$ for $\varepsilon_a > 0$ coincides with the threshold curve $U_{th}(f)$ that we obtained for the dielectric regime of MBBA with $\varepsilon_a < 0$, when the initial orientation was planar; this indicates that these instabilities are of the same nature.

The universality of the $U_{th}(f)$ curves for the cases $\varepsilon_a > 0$ and $\varepsilon_a < 0$ and, also, the fact that the instability threshold is independent of the dielectric anisotropy and of the anisotropy of the electrical conductivity suggest that the observed instability at $\varepsilon_a > 0$ and the instability of the dielectric regime at $\varepsilon_a < 0$ are of isotropic character; that is, that they are a property of the isotropic viscosity. To prove this assertion, we made measurements of the frequency dependence of the instability threshold of an MBBA mixture with $\varepsilon_a = +0.1$ at various temperatures, including ones in the isotropic phase (in the isotropic phase of NLC, the instability threshold involves a characteristic circular motion of solid foreign particles in the plane perpendicular to the direction of the electric field). The corresponding curves are shown in Fig. 3. It is evident that the character of the $U_{th}(f)$ curves is completely identical in the nematic and isotropic phases[2)]; there is no jump in the value of U_{th} on transition from one phase to the other, and the temperature dependence of U_{th} correlates with the temperature dependence of the viscosity[3)] (insert in Fig. 3). We have also observed instability in the form of circular motion in ordinary isotropic liquids. Here, with lowering of the viscosity of the liquid, U_{th} also decreases. Thus at frequency 100 Hz, $U_{th} = 90$, 7, and 2 V, respectively, for silicone oil, carbon tetrachloride, and acetone. We remark also that blocking of the electrodes by fine dielectric spacers has no effect on the character of the instability and does not change the value of U_{th}.

4. DISCUSSION OF RESULTS

The observed relations can be explained theoretically if we regard a liquid crystal as an electrolyte with electrokinetic processes inherent in it, and if we neglect the anisotropy of the medium. Here it is necessary to take into account the nonuniformity $\partial q_0/\partial z$ of the charge distribution through the specimen, which in the case of a weak electric current (and in the absence of instability) is proportional to the external voltage:

$$\partial q_0/\partial z = -\nu U/d, \qquad (1)$$

where ν is a certain coefficient representing the electro-

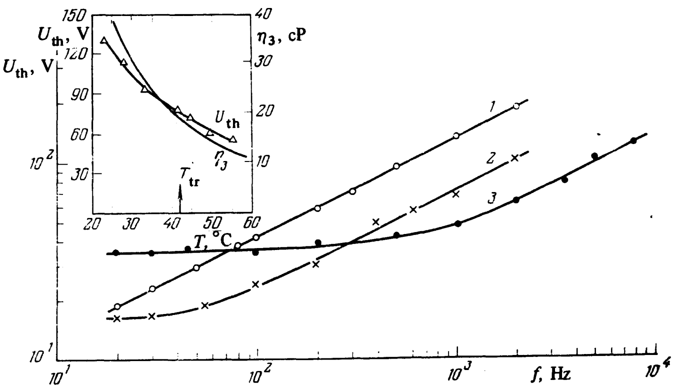

FIG. 3. Comparison of frequency dependences of the threshold of EHD instability in the nematic and isotropic phases (orientation in the nematic phase homeotropic, $\varepsilon_a = +0.1$, $d = 20$ μm). Temperatures: 23 °C (Curve 1). 41 °C (Curve 2), 55 °C (Curve 3). Insert: temperature dependence of the instability threshold (U_{th}) at frequency 1 kHz and of the mean viscosity coefficient of MBBA (η_3); T_{tr} is the temperature of transition of the liquid-crsytal phase to the isotropic.

kinetic processes,[7] and where d is the thickness of the liquid layer.[4)] It can be shown that electroconvective phenomena are important both in an isotropic medium and in a nematic when the anisotropy σ_a of the electrical conductivity is small; that is, under the condition $\nu \gg \sigma_a \gamma_1 / K_{11}$, where γ_1 is the coefficient of twist viscosity and K_{11} is the modulus of elasticity. In this case the principal cause of instability is destabilization of the charge distribution (1).

A treatment of the equations for the velocity of motion v of the liquid and for the density of volume charge (with allowance for a term $\nu E v$ that describes the entrainment of charge by the liquid flow), similar in form to that carried out in the case of the dielectric regime,[3] leads to the following results.

1. At low frequencies, the threshold field for onset of instability has the form

$$E_{th}^2 \approx 16\pi^3 \eta\sigma / \varepsilon \nu h^2, \quad \omega \ll \omega_c, \tag{2}$$

where η, σ, ε, and ν are, respectively, the viscosity, the electrical conductivity, the dielectric constant, and the effective electrokinetic coefficient (averages for NLC), and where h is the effective thickness of the layer in which there is a volume charge.

From (2) there follow two possibilities.

a) In the unipolar case[7] we have $h \sim d$, and the instability threshold voltage is

$$U_{th}^2 = (E_{th} d)^2 \approx 16\pi^3 \eta\sigma / \varepsilon\nu \approx 16\pi^3 \eta D / \varepsilon, \tag{3}$$

where $\nu \approx \sigma / D$ [7] (D is the diffusion coefficient of the charge carriers). Consequently, in this case U_{th} is independent of the thickness of the layer and of the concentration of charge carriers, that is of the electrical conductivity; this contradicts experiment.

b) In the case of charges of two signs, we have h of the order of magnitude of the Debye radius ($h^2 \sim \varepsilon D / 8\pi\sigma$). Here, therefore, we get the *field* threshold

$$E_{th}^2 \approx 128\pi^4 \eta\sigma / \varepsilon^2. \tag{4}$$

This formula describes our experimental results qualitatively: presence of a plateau on the $U_{th}(f)$ curves in the range $\omega \ll \omega_c$, proportionality of the threshold voltage to the cell thickness and to $\sigma^{1/2}$, decrease of U_{th} with decrease of viscosity, and increase of U_{th} with decrease of $\bar{\varepsilon}$.

A similar expression for the instability threshold field at constant current ($\omega = 0$) was obtained by Turnbull.[8] We remark that all the expressions for E_{th} obtained by us and by Turnbull[8] are of qualitative character, and that the numerical coefficients must be regarded with the usual caution, although they predict the order of magnitude of E_{th} correctly.

2. At high frequencies, the role of the Debye radius in the onset of instability is played by the effective diffusion length $(DT)^{1/2}$, where $T = 2\pi/\omega$ is the period of the external field. In this case we have

$$E_{th}^2 \approx \frac{16\pi\eta\sigma}{\varepsilon\nu} \frac{\omega}{D} \approx \frac{16\pi\eta\omega}{\varepsilon}, \quad \omega \gg \omega_c. \tag{5}$$

In agreement with experiment, it follows from (5) that the threshold field is proportional to $\omega^{1/2}$, is independent of the value of the electrical conductivity, and decreases with decrease of the viscosity.

Thus it may be concluded that instability in a homeotropically oriented NLC with $\varepsilon_a > 0$ (and, for a definite set of parameters, also in the case $\varepsilon_a < 0$ at frequencies $\omega \gg \omega_c$; that is, in the so-called dielectric regime) is caused by electroconvective processes in the liquid and is of "isotropic" character. This means that for its occurrence the anisotropic properties of the material are unimportant, and the role of the liquid crystal reduces merely to visualization of the instability by virtue of the optical anisotropy. The character of the vortex motion of the liquid and, also, the form of the domain patterns depend on the orientation of the NLC director because of the anisotropy of the viscous and optical properties of the latter. In the isotropic phase, the instability is realized in comparatively simple form: as circular vortices, whose axis coincides with the direction of the electric field.

The authors express their thanks to E. A. Kirsanov for providing the detailed results of his experiments, and also V. G. Chigrinov and M. F. Grebenkin for useful discussions.

[1)]In the case of an initial planar orientation, the initiation of a similar instability (with a somewhat different form of domain patterns) is preceded by a process of reorientation of the director (the Frederiks transition).

[2)]The similarity of the frequency behavior of the instability threshold voltage in the nematic and isotropic phases of NLC has been noted also by Kirsanov.[5]

[3)]Dilution of MBBA, in order to change the dielectric anisotropy, up to CEHBA concentrations of the order of 15 wt% ($\varepsilon_a \approx +3$) has practically no effect on the value of the viscosity of the mixture.

[4)]We disregard injection of charge carriers from the electrodes, but we allow for nonuniformity of the distribution of intrinsic charge carriers in the electric field.

[1]L. M. Blinov, Usp. Fiz. Nauk **114**, 67 (1974) [Sov. Phys. Usp. **17**, 658 (1975)].

[2]E. Dubois-Violette, P. G. de Gennes, and O. Parodi, J. Phys. (Paris) **32**, 305 (1971).

[3]I. W. Smith, Y. Galerne, S. T. Lagerwall, E. Dubois-Violette, and G. Durand, J. Phys. (Paris) **36**, C1-237 (1975).

[4]P. G. de Gennes, Commun. Solid State Phys. **3**, 35 (1970).

[5]E. A. Kirsanov, Uch. zap. Ivanovskogo Gos. universiteta **128**, 59 (1974).

[6]R. A. Kashnow and H. S. Cole, Mol. Cryst. Liq. Cryst. **23**, 329 (1973).

[7]L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Fizmatgiz, 1959 (translation, Pergamon Press and Addison-Wesley, 1960).

[8]R. J. Turnbull, J. Phys. D **6**, 1745 (1973).

Translated by W. F. Brown, Jr.