2)There are, for example, known experiments on adsorption of W on W wherein the adsorbed W is significantly electropositive.[13]

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Electrohydrodynamic instability with isotropic mechanism in cholesteric liquid crystals

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It is shown that the "dielectric" regime in cholesteric liquid crystals with negative dielectric anisotropy, as well as the newly-observed electrohydrodynamic instability in cholesteric liquid crystals with positive dielectric anisotropy, which arise in a planar texture and at voltages above the threshold of the unwinding of the cholesteric helix as well as in confocal textures, are manifestations of an isotropic instability due to electroconvective phenomena inherent in ordinary electrically conducting liquids. The role of the liquid crystal reduces to visualization of the elctrohydrodynamic currents as a result of the anisotropy of the refractive index, and to an influence exerted on the current topology by the anisotropy of the viscosity.

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When an electric field is applied parallel to the helix axis in the planar texture of a cholesteric liquid crystal (CLC), an instability appears at a certain threshold voltage, in the form of spatially-periodic deformations that are two dimensional (of the square grid type) at thickness d greatly exceeding the helix pitch $P_0 (d \gg P_0)$,[1,2] and one-dimensional at $d \approx P_0$ (Ref. 3). For CLC with positive dielectric anisotroy ($\Delta\varepsilon > 0$) the instability sets in at arbitrary external-field frequencies, whereas for CLC with $\Delta\varepsilon < 0$ it appears only below a certain critical frequency f_{cr}. This instability is similar to the Fréedericsz transition and Williams domains in nematic liquid crystals (NLC); its causes, just as in the case of NLC, are the destablizing moments of the forces induced by the field as a result of the anisotropy of the dielectric constant and (or) the anisotropy of the electric conductivity of the CLC. The threshold voltage of this instability, naturally, depends strongly on the magnitude and sign of the dielectric anisotropy, on the electric-conductivity anisotropy, and on the pitch of the helix, and is well described by the Helfrich-Hourault theory.[4-6]

For the same geometry, in CLC with $\Delta\varepsilon < 0$, and at frequencies higher than f_{cr}, deformations were observed[1,2] with a much smaller period (the analog of "chevrons" in NLC). So far, there are no published suggestions concerning the possible mechanism of this electrohydrodynamic (EHD) instability, which is called, just as in the case of NLC, the "dielectric" regime. Nor is it clear whether this mechanism is anisotropic, i.e., whether it is due to the anisotropy of the CLC properties, just as, e.g., the Helfrich-Houralt mechanism.

There is also a need for explaining the causes of the EHD instabilities observed by us in part[7] in CLC with $\Delta\varepsilon > 0$ in a planar structure and at voltages higher than the threshold of the untwisting of the cholesteric helix, and also in a confocal texture at any sign of $\Delta\varepsilon$. These cases were previously regarded as electrohydrodynamically stable.[8,9]

The present work was stimulated also by researches[10,11] that have shown that the EHD instabilities that manifest themselves in NLC in the form of "chevrons" and other patterns are caused by electroconvective motion of the liquid, and the instability mechanism is isotropic, i.e., it is not due to the anisotropy of the electric properties of the NLC.

Our present task is to show that the dielectric regime in the planar texture of CLC with $\Delta\varepsilon < 0$, and the observation of EHD instability in other textures and in CLC with $\Delta\varepsilon > 0$, can be explained with the aim of the very

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same isotropic mechanism. This is accomplished by proving that the threshold voltage of these instabilities is independent of such anisotropic CLC parameters as the dielectric anisotropy, the electric-conductivity anisotropy, and the pitch of the helix.

EXPERIMENTAL PROCEDURE

The frequency dependences of the threshold voltage U_{thr} at which instabilities of various kinds appear in a CLC layer were recorded with a polarization microscope in planar or wedge sandwich cells. The accuracy with which U_{thr} was measured was 5–10%. Unless specially stipulated, the observations were made at room temperature. The planar orientation of the CLC molecules on the walls of the cell was ensured by rubbing by the Chatelain method, and the homotropic orientation was produced by deep purification of the SnO_2 electrodes.

The liquid crystals were mixtures of nematic substances (p-n-methoxybenzylidene-p′-butylaniline (MBBA) or p-n-butyl-p′-methoxyazoxybenzene (BMAOB)) with cholesteryl oleate or cholesteryl caprinate, with a cholesteric-helix pitch from 50 to 1 μm. To obtain an electric conductivity in the range $10^{-11} < \sigma_{\parallel} < 10^{-8}$ ($\sigma_{\parallel}$ is the electric conductivity in the direction parallel to the director), the mixtures were doped with tetrabutyl ammonium bromide. Variation of the dielectric anisotropy of the mixtures in a range $-1 < \Delta\varepsilon < +8$ was ensured by doping the initial mixtures of the compounds with large longitudinal (p′- cyanophenyl ester of p-heptyl benzoic acid) and large transverse (2, 3-dicyano-4-amyl oxyphenyl ester of p-amyl oxybenzoic acid) dipole moments.

RESULTS AND THEIR DISCUSSION

Figure 1 shows the frequency dependence of the threshold voltage at which instability sets in a planar CLC texture with $\Delta\varepsilon < 0$, the solid line corresponding to the so-called dielectric regime, and the dashed lines to the anisotropic instability due to the Helfrich-Hurault mechanism. The forms of these instabilities at various ratios of the layer thickness to the helix pitch is shown in Figs. 2a–2d. It is seen from Fig. 1 that a fourfold change of $\Delta\varepsilon$ and a 30-fold change of the electric conductivity does not affect the threshold of the dielectric regime, but alters greatly the threshold of the anisotropic instability. The threshold of the dielectric regime is likewise not affected by the anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ of the electric conductivity, a fact established by a separate experiment.

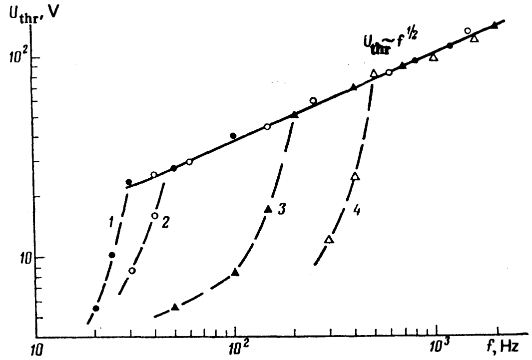

FIG. 1. Frequency dependences of the threshold voltage U_{thr} of EHD instabilities for a planar CLC texture with $\Delta\varepsilon < 0$ (BMAOB + cholesteryl oleate, $d = 24$ μm, $P_0 = 40$ μm). Curve 1: $\sigma_{\parallel} = 5 \cdot 10^{-11}\ \Omega^{-1}\text{cm}^{-1}$, $\Delta\varepsilon = -1$. Curves 2–4 ($\Delta\varepsilon = -0.25$): $\sigma_{\parallel} = 5 \cdot 10^{-11}$ (2), $\sigma_{\parallel} = 5 \cdot 10^{-10}$ (3), $\sigma_{\parallel} = 1.5 \cdot 10^{-9}$ (4) $\Omega^{-1}\text{cm}^{-1}$.

Figure 3 shows the dependence of the threshold U_{thr} of the dielectric regime on the number of the Grandjean zone (the measurements were made in cells of fixed thickness with a concentration gradient of the cholesteric component in the mixture), and the pitch of the helix changes here from 50 to 1 μm. In the case of the anisotripic mechanism of the dielectric regime, the pitch of the helix would play an important role and so large a variation of its value would undoubtedly change U_{thr} radically. In our case, however, U_{thr} increased by only

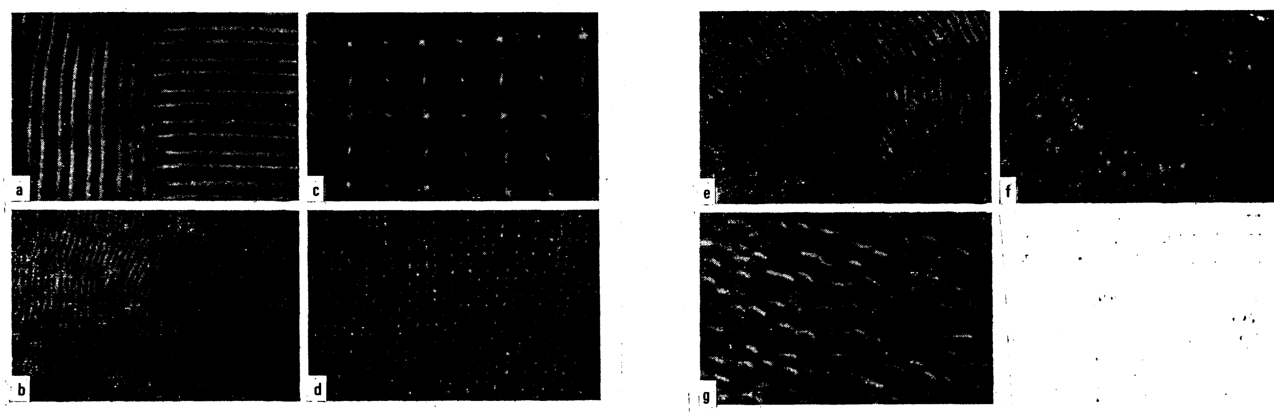

FIG. 2. Typical instabilities in CLC. Anisotropic instability in a planar texture: a) layer thickness d of the order of the helix pitch P_0 ($d \approx P_0$), photograph of the boundary between the first and second Grandjean regions; b) $d \gg P_0$. Isotropic instability in planar texture: c) $d \approx P_0$; d) $d \gg P_0$. Isotropic instability produced after untwisting of the cholesteric helix: e) $f < f_{cr}$; f) $f > f_{cr}$, homotropic orientation of the molecules on the glasses; g) $f > f_{cr}$, planar orientation of the molecules on the glasses. Photograph dimensions: a–d) 120 × 80 μm; e–g) 480 × 310 μm.

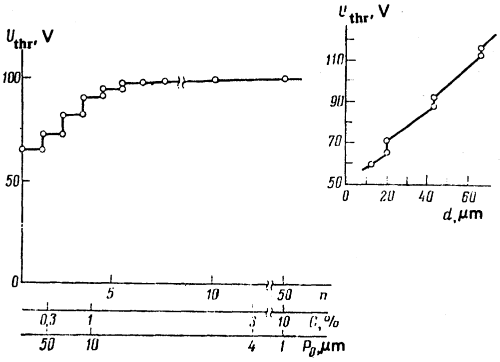

FIG. 3. Dependence of the threshold voltage U_{thr} of the dielectric regime on the number n of the Grandjean zone (the abscissas are the corresponding values of the equilibrium helix pitch P_0 and of the concentration C of the cholesteryl caprinate in the MBBA): $d=24$ μm, $f=250$ Hz. Insert—dependence of the threshold of the dielectric regime on the CLC layer thickness (MBBA + 0.3% cholesteryl caprinate, $P_0=50$ μm, $f=250$ Hz).

50%, owing to the increase of the viscosity of the mixture.

The fact that the threshold of the dielectric regime is independent of the anisotropy of the electric properties ($\Delta\varepsilon$ and $\sigma_{\parallel}/\sigma_{\perp}$) and, indirectly, of the pitch of the helix, is evidence that the mechanism of this instability is isotropic and is not due to the anisotropy of the CLC or associated apparently, as in NLC,[10,11] with electroconvective phenomena in the liquid in an inhomogeneous field. The role of the liquid crystal reduces to visualization of the EHD currents due to the anisotropy of the refractive index and to the effect exerted on the topology of these currents by the viscosity anisotropy.

In particular, the differences between the optical patterns of the dielectric regime in different Grandjean bands (compare photographs c and d in Fig. 2) is due to the different topology of the EHD currents, a topology determined, in view of the viscosity anisotropy, by the distribution of the director in the layer, which is different for the different bands. It is of interest that the patterns of the isotropic and anisotropic instabilities in a planar texture are similar (cf. photographs a with c and b with c in Fig. 2).

The jumps of U_{thr} in the transitions between the Grandjean bands (Fig. 3) are explained as being due to changes of the apparent viscosity, whose magnitude, in view of the penetration effect,[12] depends on the helix pitch, which changes jumpwise in the transitions between the bands.[3] The same jumps appear also on the plot of U_{thr} against the thickness d of the layer (the measurements were made in wedge-like cells, see the insert of Fig. 3), although on the average the threshold is field-dependent ($U_{thr} \sim d$).

Naturally, isotropic instability exists also at frequencies $f<f_{cr}$, but it is masked there by the anisotropic instability, whose threshold is usually lower.

Since the dielectric regime that exists in the planar texture of CLC with $\Delta\varepsilon<0$ is now assumed to be a manifestation of the isotropic instability, it is of interest to investigate the manifestations of this instability in other textures and in CLC with $\Delta\varepsilon \geq 0$.

The most interesting cases are illustrated in Fig. 4, which shows the frequency dependences of the threshold voltages of the EHD instabilities for different textures and different $\Delta\varepsilon$, but with unchanged layer thickness or concentration of the cholesteric component in the mixture.

1) $\Delta\varepsilon \geq 0$, planar texture. In this case, for an isotropic instability to manifest itself directly in a planar texture, the threshold of the anisotropic instability must be raised above the threshold of the isotropic instability at least for several frequencies, as was in fact accomplished here by choosing the values of $\Delta\varepsilon$. Curve 1 corresponds to the case when isotropic instability appears at low frequencies ($f<250$ Hz) and anisotropic at high frequencies ($f>250$ Hz). It is of interest to compare this situation with the case $\Delta\varepsilon<0$, where an anisotropic instability is usually observed at low frequencies and an isotropic one at high ones. Curve 2 illustrates the case when isotropic instability sets in at medium frequencies (40 Hz $<f<$ 70 Hz) and anisotropic at low ($f<40$ Hz) and high ($f>70$ Hz) frequencies. In all cases when the isotropic instability appears in a planar texture, it takes the form shown in Figs. 2b and 2d (regardless of the sign of $\Delta\varepsilon$).

2) The isotropic instability has an optically well pronounced threshold also in the homotropic nematic texture obtained in CLC with $\Delta\varepsilon>0$ at voltages above the threshold of the cholesteric-helix untwisting. This situation was realized by us likewise by selecting the value of $\Delta\varepsilon$. Curve 3 shows the helix-untwisting threshold under conditions of homotropic orientation of the molecules on the glasses of the cell (the initial texture was confocal in this case). The isotropic instability set in at a threshold voltage whose frequency dependence is rep-

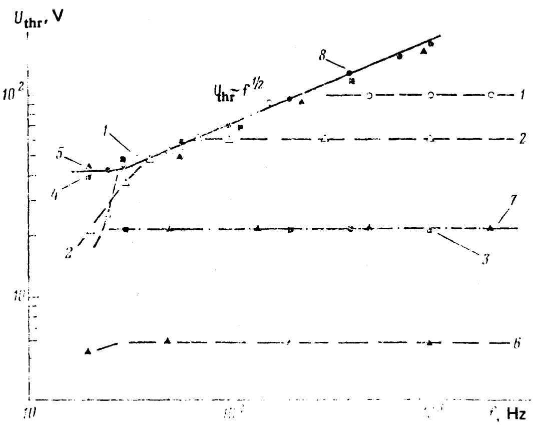

FIG. 4. Frequency dependences of the threshold voltages U_{thr} of the EHD instabilities for various textures and various $\Delta\varepsilon$: $d=24$ μm, $P_0=3$ μm. The solid curve corresponds to isotropic EHD instability, the dashed to anisotropic instabilities, and the dash-dot to the threshold of helix untwisting (planar orientation, ●—$\Delta\varepsilon=-0.5$, ○—$\Delta\varepsilon=+0.01$, △—$\Delta\varepsilon$ $+0.02$, ▲—$\Delta\varepsilon=+2$; homotropic orientation of the molecules on the glasses, ■—$\Delta\varepsilon=+2$.

resented by curve 4, on which one can see two regions: a flat region at frequencies lower than f_{cr}, and a region with a square-root dependence ($U_{thr} \propto f^{1/2}$) at frequencies $f > f_{cr}$ (the form of the instability in these regions is represented in Figs. 2e and 2f, respectively). A similar character is possessed by curve 5, which coincides with curve 4 and gives the frequency dependence of the threshold of the isotropic instability for the same mixture in the case of "planar" boundary conditions. The formation of the confocal texture is preceded here by the anisotropic instability (curve 6), and the threshold of the untwisting of the helix (curve 7) coincides with the untwisting threshold for the "homotropic" boundary conditions. The form of the isotropic instability at the frequencies $f > f_{cr}$ in the nematic layer obtained after the untwisting of the helix, under planar boundary conditions (Fig. 2g), differs from the case of homotropic boundary conditions, thus pointing to a strong influence of the boundary layers of the liquid on the topology of the EHD currents.

3) Isotropic instability has set in also in a confocal structure (observed as a liquid motion under a microscope) for all boundary conditions and at any sign of $\Delta\varepsilon$.

In all the described cases, the voltages U_{thr} at which the isotropic instability set in coincided with the threshold of the dielectric regime (curve 8 on Fig. 4) and were independent of the anisotropic parameters of the CLC ($\Delta\varepsilon, \sigma_{\parallel}/\sigma_{\perp}, P_0$), thus pointing once more to a single isotropic mechanism of these instabilities. With rising temperature, U_{thr} decreased in accord with the decrease of the viscosity, and this quantity experienced no jump on going to the isotropic phase (in the isotropic phase, the instability threshold corresponds to the start of circular motion of the solid extraneous impurity particles in a plane perpendicular to the electric-field direction).

Thus, in CLC there exists an isotropic EHD instability, and its threshold voltage, as a function of frequency, is described by curves such as 4 and 5 in Fig. 4. We assume that this instability is due to electroconvective phenomena caused by a space-charge gradient (and accordingly by a field inhomogeneity) directed along the external field. In fact, the expressions for the threshold of this instability, obtained in Refs. 10 and 11:

$$U_{thr} \sim \eta^{1/2}\sigma^{1/2} d/\varepsilon \quad \text{if } f < f_{cr}$$
$$U_{thr} \sim \eta^{1/2} f^{1/2} d/\varepsilon^{1/2} \quad \text{if } f > f_{cr}$$

(where η, σ, and ε are respectively the average values of the viscosity coefficient, of the electric conductivity, and of the permittivity of the liquid) account qualitatively for the experimentally observed dependences of the threshold of the isotropic instability in CLC on the indicated parameters.

Our principal results are therefore the following: EHD instabilities are produced in planar-texture CLC with $\Delta\varepsilon \geq 0$, at voltages below the threshold of the untwisting of the cholesteric helix, as well as in confocal textures at any sign of $\Delta\varepsilon$. It is shown that the threshold voltage for the appearance of these instabilities and of the previously known dielectric regime in CLC with $\Delta\varepsilon < 0$ does not depend on anisotropic CLC parameters such as the conductivity anisotropy, the dielectric anisotropy, the ptich of the helix, or the distribution of the director in the layer. It is concluded that these instabilities are a manifestation of isotropic instability due to electroconvective phenomena in CLC, just as in an ordinary electrically conducting liquid. The role of the liquid crystal reduces to a visualization of the EHD currents on account of the anisotropy of the refractive index, and to an effect exerted on the topology of these currents by the anisotropy of the viscosity.

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