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INVESTIGATION OF THE NEMATIC–FERROELECTRIC INTERFACE UNDER A STRONG MAGNETIC FIELD

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The behaviour of methoxy benzylidene butyl aniline (MBBA) nematic liquid crystal on the cleavage surface of triglycine sulphate under a strong magnetic field has been investigated. With the saturation regime obtained for the liquid crystal cell in fields up to 100 kOe, for the first time the possibility appears to determine not only the ordinary anchoring coefficient W_2, but the effective anchoring energy W^* without any fitting procedure. Considerable difference in these parameters (two orders of magnitude) disagrees with "electrical" corrections of the Rapini–Papoular approximation. This discrepancy is connected with the surface polarization caused by spontaneous ordering of longitudinal components of MBBA molecular dipoles on interface. The form of the anisotropic interaction potential for such interfaces has to take into account polar effects in near-surface layers of the liquid crystal.

Keywords: A. ferroelectrics, A. liquid crystals, A. surfaces and interfaces, D. phase transitions, E. light absorption.

1. INTRODUCTION

Studying the interactions between nematic liquid crystals (LC) and cleavages of ferroelectric ones is especially interesting due to possible effects caused by polar symmetry of LC–substrate interface [1]. According to theoretical analysis the polarization, arising at LC-wall contact, can give essential contribution to the surface anchoring energy only when the substrate electric field is very large [2]. An attempt to estimate the effect of surface polarization on the anchoring energy of methoxy benzylidene butyl aniline (MBBA) towards triglycine sulphate (TGS) cleavage in hybrid cell was taken in [3]. No polar effects were detected under the given experimental conditions. Anchoring energy between planarly oriented MBBA layer and the TGS cleavage surface was determined by us from the threshold field of Freedericksz transition [4]. Its value $W_2 = 1 \cdot 10^{-4}$ erg/cm^2 was calculated in terms of Rapini–Papoular approximation. At this weak anchoring the complete reorientation of nematic director would be to take place near Freedericksz threshold. According to our preliminary studies the magnetic field dependence of intensity of probing laser radiation above the threshold disagrees with this. It would be natural to study LC at strong fields up to saturation when all nematic layers including surface polarized ones were reoriented. Note that these few experiments [5–7] are restricted in using strong electric fields due to parasitic effects and by difficulty to reach the saturation magnetic field.

In this connection, the present paper is devoted to studying MBBA behaviour on TGS cleavages by means of technique [4] at large director distortions. The effective anchoring energy W^* has been found from the saturation magnetic field. Within correlation of anchoring energy values obtained at weak and strong distortions of LC layers in wide range of applied field the cotribution of dipole mechanism of polarization into surface potential is discussed.

2. EXPERIMENTAL

Planar MBBA layers under study were doped by dichroic anthraquinone dye AQ-10 and placed between two coaxial TGS substrates with "-" domains. Director **n** of MBBA is parallel to crystallographic c-axis of TGS. Cell parameters and technique of sample preparation are the same as in [4].

The cell is centred into channel of Bitter solenoid generating the strong magnetic fields up to 120 kOe. Thermostatic insert prevents the sample heating by solenoid and allows to maintain temperature $(23 \pm 0.2)^{o}$C for the whole magnetic field range. Magnetic field was scanned from 0 till 100 kOe with 4 kOe/min. Slow scanning velocity allows to minimize experimental errors due to LC inertness. Magnetic field measuring errors due to solenoid's powering current instabilities and pulsations did not exceed 0.3 %. Polarized He–Ne laser beam has run along the solenoid channel parallel to its magnetic force lines and penetrates the sample normally to TGS substrates. Plane of beam polarization has coincided with director of undistorted LC.

Dependence of intensity I on magnetic field H caused by change of solute MBBA absorption is given in X–Y recorder pattern (Fig. 1). As seen from the figure, intensity $I(H)$ varies between two mark values of transmission intensity of planar sample $I_{\|}$ and $I_{\perp}$ at director orientation being parallel and perpendicular to penetrating light polarization vector **e**, respectively. Relative photometric error $\Delta I/I$ does not exceed $1.5 \div 2.0$ %. Sharp initial deviation of $I(H)$ curve from $I_{\|}$ corresponds to threshold field of Freedericksz transition, whose value $H = 0.7$ kOe coincides with our former one obtained by means of electromagnet [4]. In the strong field region the dependence $I(H)$ approaches the mark $I_{\perp}$ and reaches it at certain critical field $H = 62.4$ kOe. Since perpendicular components of transmission intensity for planar and homeotropic LC orientations are equal, that apparently this critical field corresponds to saturation one H_{sat}. This is also approved by unchange of intensity signal at switching the orientation of polarization vector from $\mathbf{e} \parallel \mathbf{c}$ till $\mathbf{e} \perp \mathbf{c}$, being peculiar for homeotropic LC texture. Thus magnetic field applied to the sample converts it to homeotropic state. On further increasing the magnetic field up to 100 kOe the curve $I(H)$ does not deviate from mark level $I_{\perp}$. Asymptotic character of $I(H)$ leads to an error in determining the saturation field, having been taken into account: $H_{sat} = 62.4 \pm 1.6$ kOe.

3. RESULTS AND DISCUSSION

To calculate the anchoring energy, the expression for total director reorientation at the saturation field was used [8]

$$\coth\left(\frac{\pi}{2}\frac{H_{sat}}{H^{\infty}}\right) = \frac{\pi K_{33}}{W^{*} d}\frac{H_{sat}}{H^{\infty}} \qquad (1)$$

where W^{*} is the sum coefficients for expansion of surface potential

$$F_s = \frac{1}{2}W_2\cos^2\theta + \frac{1}{2}\sum_{n=2}^{\infty} W_{2n}\cos^{2n}\theta \qquad (2)$$

into the series by even degrees of Legendre polynomials; θ is the angle of director orientation relatively to surface normal; $H^{\infty} = \pi/d(K_{11}/\Delta\chi)^{1/2}$ is the threshold magnetic field corresponding to infinite strong anchoring LC–substrate; d is the sample thickness; K_{11}, K_{33} are Frank constants for splay and bend deformations, respectively; $\Delta\chi$ is anisotropy of magnetic susceptibility. The meanings of these parameters are the same as in [4]. Having substituted the value H_{sat} into the expression (1) one can obtain $W^{*} = (2,1 \pm 0,1)\cdot 10^{-2}$ erg/cm^2. Thus the present paper gives the evidence to determine W_2 and W^{*} parameters during the same experiment.

Note that the meaning W^{*} did not obtain in [5], since magnetic field $H = 100$ kOe turned to be insufficient for reorientation of homeotropic ordered MBBA on glass substrates into the planar state. Threshold field of Freedericksz transition and saturation one were given in [6] for the same experiment. Nevertheless, none of these parameters permits to calculate proper values of anchoring energy: W_2 — due to strong anchoring between planar layer 5CB and glass surfaces, W^{*} — due to large error in determination of saturation field arising from strong electric field usage. The meaning W^{*} only for planar layers 5CB on glass surfaces was obtained in [7]. Experience [5–7] shows that contribution of higher-rank terms, partially $\cos^4\theta$ into phenomenological expansion of LC–substrate interaction potential, in addition to second-rank term of Rapini–Papoular expression, does not exceed 10 %. This contribution can be connected with order-electric polarization [9].

Difference by two orders for values W_2 and W^{*} obtained from dependence $I(H)$, Fig. 1, appears to be surprising, because the surface potential in Rapini–Papoular form must remain relatively correct for large deviations of nematic director from its initial orientation [9].

Figure 2 represents dependencies of reduced threshold field of Freedericksz transition $h' = H_{th}/H^{\infty}$ and

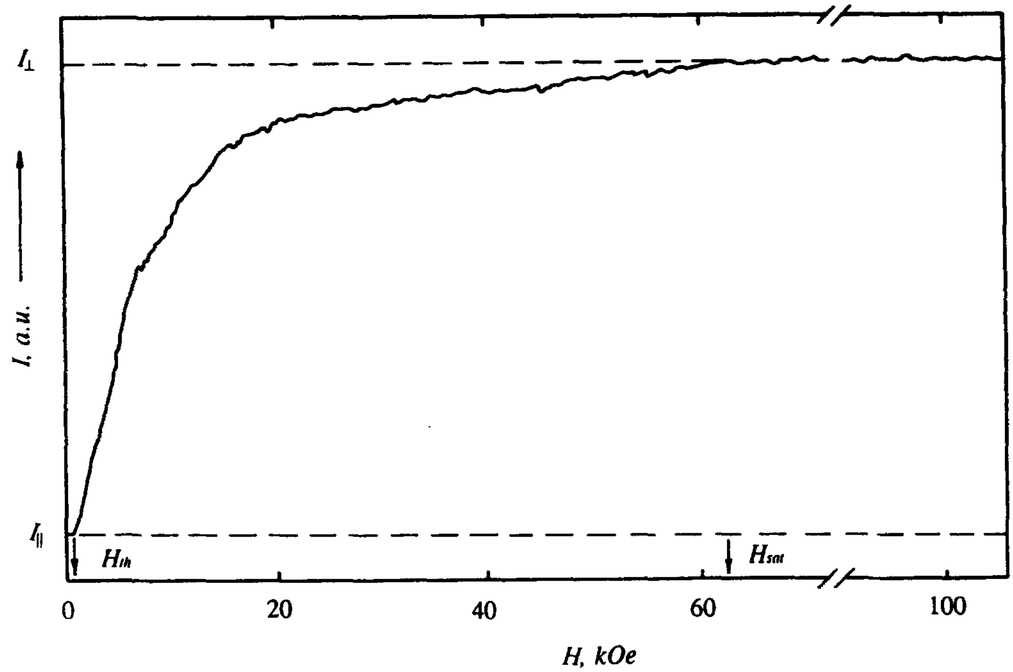

Fig. 1. X–Y recorder pattern for MBBA–TGS "-" domain cell: solid line — dependence $I(H)$; dotted lines — transmission intensities $I_\parallel$ and $I_\perp$ for the 30 μm undistorted planar sample. Arrows indicate critical values of magnetic field.

saturation field $h'' = H_{sat}/H^\infty$ on parameter $\beta = Wd/\pi K_{33}$ for MBBA nematic at fixed layer thickness d. The function $h'(\beta)$ is calculated in terms of Rapini–Papoular approximation, and $h''(\beta)$ — by (1) in assuming $W_2 \sim W^* \sim W$. The figure demonstrates that at $W = 1 \cdot 10^{-4}$ erg/cm^2 the threshold fields might actually coincide. It means in physical sense, that nematic layer ought to reorient as a whole. At $W = 2,1 \cdot 10^{-2}$ erg/cm^2 the threshold must be distinct quite by far, and so the experiment reveals. Probably experimental value of threshold field is understated against the foreseeing one.

An important feature of TGS cleavage is the presence of high surface electric field owing to spontaneous polarization of the ferroelectric. This field is responsible for ordering the LC molecules [10]. Polar symmetry of LC–substrate interface and amphiphilic character of MBBA molecules lead to surface polarization effects [11]. Note that value of average polarization density in [11] corresponds to homeotropic MBBA layer with highly ordered longitudinal components of molecular dipoles. At MBBA interaction with TGS surface this value is apparently quite less, because the strong electric field of the substrate tends to align MBBA molecules in cleavage plane and to destroy polar ordering of near-surface LC layer. On the other hand, a polar contribution into the potential can be substantial namely owing to strong field.

According to Parsons model [12], the surface potential may be written in the form of competing contributions: short-range polar one $W_1 \cos\theta$ (homeotropic) and long-range dielectric one $W_2 \cos^2\theta$ (planar). This competition takes place even for $W_1 \ll W_2$. Interaction between MBBA and TGS cleavage apparently falls under the present instance, because, on the one hand, W_2 and W^* disagree in term of (2), and on the other hand, the threshold character of Freedericksz transition reveals clearly. This testifies to small pretilt (if it exists) in LC layer. Evidently the pretilt leads to considerable threshold curving observed experimentally for MBBA cells placed between two coaxial TGS plates with "+" domains.

The surface potential taking into account the polarization effects for large angle deflections from "easy" axis has written as

$$F_s = -W_1 \cos\theta + \frac{1}{2}\sum_{n=1}^{\infty} W_{2n} \cos^{2n}\theta. \qquad (3)$$

An attempt [13] was made to connect experimental values of critical fields with anchoring parameters by minimizing free energy of LC under the boundary conditions (3). It has been shown, that linear term

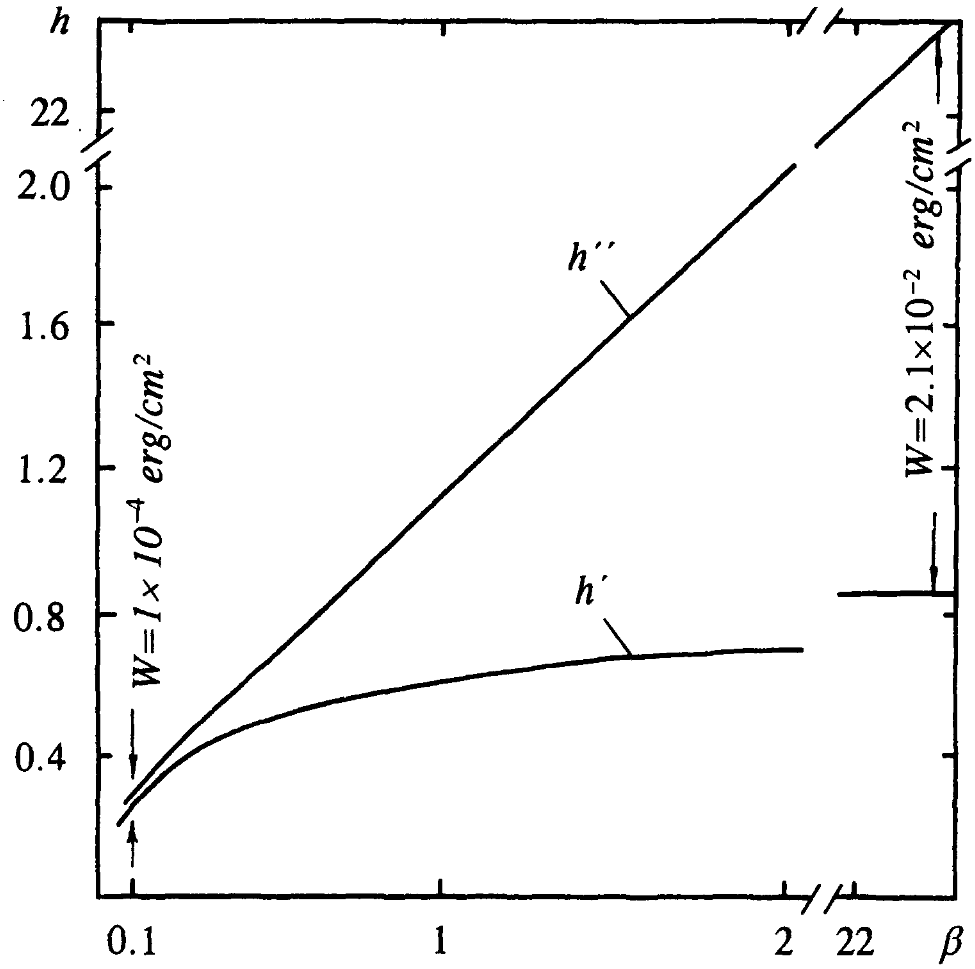

Fig. 2. Calculated dependencies of reduced magnetic field h on parameter β. h' is threshold field of Freedericksz transition, h'' is the saturation field.

can substantially reduce the threshold field of Freedericksz transition at small distortions of director field. Expression similar to (1) has been obtained for large distortions, where $W^* = -W_1 + W_n$, $W_n = \sum_{n=1}^{\infty} nW_{2n}$. At $W_1 \ll W_n$ the saturation field is not renormalized.

It is worthwhile to note, that surface polarization model [2] where the vector **P** = *const* is always normal to the surface, and model [14], where $\mathbf{P} \sim \mathbf{P}(\cos\theta)$ are both leading to the same result: polar contribution is incorporated by square term of surface potential. As noted above, in this instance our experiment meets the explanation difficulties.

4. CONCLUSION

Interaction between nematic liquid crystal and cleavage surface of ferroelectric one at strong magnetic field has been investigated. Weak anchoring between MBBA and TGS cleavage gave a possibility to determine the anchoring energy both from critical field of Freedericksz transition and from saturation field. Substantial difference in these values can be caused by presence of two competing factors — the long-range electric field of the substrate and the short-range effects of surface polarization. The latter renormalizes the anchoring energy obtained by nematic deformations near the initial planar LC orientation and does not reveal actually at nematic reorientation into homeotropic state by outer field. So the energy value calculated from saturation field can be a featuring parameter for nematic–substrate interactions.

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