Electrohydrodynamic Instabilities in Some Nematic Azoxy Compounds with Dielectric Anisotropies of Different Sign

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Electrohydrodynamic instabilities are observed in planar slabs of nematic azoxy compounds with values for $\Delta\epsilon=\epsilon_{||}-\epsilon_{\perp}$ between -0.2 and $+0.2$. Above a threshold voltage for negative $\Delta\epsilon$ the well-known cellular domain pattern is found. For positive $\Delta\epsilon$ a reorientation only is observed in the nematic phase. However, for dc fields at the same voltage, cellular flow is present in the isotropic phase. Moreover, in this case domains can be introduced by a magnetic field $H\perp E$. These different effects cannot be explained by considering stability criteria only. A discussion is given in which the orientating torques of the field on the nematic determine whether an instability leads to domains or not.

I. INTRODUCTION

The anisotropy in the molecular magnetic susceptibility of a nematic liquid crystal is usually found to be positive: $\Delta\chi=\chi_{||}-\chi_{\perp}>0$ where $\chi_{||}$ and $\chi_{\perp}$ are defined parallel and perpendicular to the preferred axis. Consequently a nematic will be aligned with the long molecular axis parallel to the external magnetic field. On the other hand, the anisotropy in the static dielectric constant ($\Delta\epsilon$) can have either sign. Hence orientations with the molecular axis parallel to the field (positive $\Delta\epsilon$) and perpendicular to the field (negative $\Delta\epsilon$) can be expected. However, *p*-azoxyanisole (PAA) and other compounds with negative $\Delta\epsilon$ have often been found to align parallel to the field.[1] Taking the conductivity into account this anomalous alignment has been explained as a dynamic effect.[2,3] Alignment can also be achieved without external fields. When a thin layer of a nematic is put between rubbed glass plates, the molecular axis is found to be parallel to the rubbing direction.

The effect of an electric field perpendicular to a rather thin (10–100 μm) layer of a nematic liquid crystal sandwiched between planar electrodes has been studied extensively for $\Delta\epsilon<0$. Above a threshold V_c (in the dc case 5–8 V) microscopically a stationary domainlike pattern is observed.[4] When the voltage is increased this "laminar" flow pattern[5] gradually changes into a regime of "turbulent" flow in which the liquid crystal scatters light[6] strongly. There are, however, some important differences between ac and dc excitation: (a) The dc effect exists only when the electrodes inject charge carriers into the fluid.[6] In the ac case this is not necessary since the effect is also observed when the electrodes are separated from the nematic by thin insulating sheets.[7] (b) In the dc case cellular flow is also found above the clearing temperature T_c,[8] while the ac effect disappears at this point.[7]

In this paper we present contrasting experimental results for nematics with $\Delta\epsilon>0$ and $\Delta\epsilon<0$. It will be shown that the orientating torques on the nematic by the electric field and eventually by a magnetic field determine whether a hydrodynamic instability becomes visible as a domain pattern, or whether only a reorientation is observed.

II. BASIC THEORY

In connection with electrohydrodynamic instabilities several theoretical papers have been published. In the theory of Felici[9] a net injection of electrons from one of the electrodes into a low conductivity liquid leads to space charges. By exchange of momentum the force exerted on the space charges is transferred to the liquid which gives a cellular hydrodynamic flow analogous to the classical Bénard problem.[10] In a nematic this flow pattern can be observed microscopically (domains). This model is restricted to the dc case because all injection disappears above a few hertz. As the experimental threshold voltages for the cellular flow in isotropic dielectrics[11] are of the same order of magnitude as in nematics, the behavior of a nematic liquid crystal in a dc electric field above and below T_c can, in principle, be understood in this way. However, then one would expect that the results do not depend on typical nematic quantities as, e.g., $\Delta\epsilon$.

In a nematic, space charges can also arise from a different origin. One would expect that (radical) ions have a greater mobility in the direction of the molecular alignment, leading to an anisotropy in the conductivity: $\sigma_{||}>\sigma_{\perp}$. Carr has pointed out[2] that when a nematic with anisotropic conductivity is placed in an electric field, deviations from a uniform orientation lead to positive and negative space charges.

Irrespective of their origin (injection or anisotropy in σ) the space charges will interact with the field which causes material flow. The flow is accompanied by shear which, in turn, exerts a torque on the molecules of the nematic liquid. On the other hand the space charges also influence the torque due to the normal dielectric alignment through the internal fields which they produce in addition to the external field. Helfrich[3] has made detailed calculations of the torques involved. For a dc electric field perpendicular to the molecular axis

TABLE I. Electric characteristics of the nematic liquid crystals used.

Compound	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	σ ($\Omega^{-1}\cdot cm^{-1}$)	$\sigma_{\parallel}/\sigma_{\perp}$	ξ [Eq. (2)]
N4	5.1	5.3	10^{-9}	1.6	0.5
DIBAB	4.2	4.0	10^{-10}	1.2	0.4
N4/DIBAB	4.6	4.6	5×10^{-10}	1.4	0.4

(i.e., stabilized by the walls or a magnetic field $H\perp E$) the threshold *field* E_c is given by the expression[3]

$$-\xi E_c^2/4\pi+q^2k_{33}+\Delta\chi H^2=0. \quad (1)$$

k_{33} is the elastic constant for bend ($k_{33}>0$). Usually the wave vector q of the distortion is taken inversely proportional to the thickness of the sample and then a threshold *voltage* V_c is predicted. Further

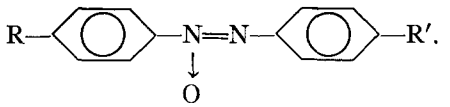
$$\xi=\Delta\epsilon(\sigma_{\perp}/\sigma_{\parallel})+(\kappa_1/\eta_1)\epsilon_{\parallel}[(\epsilon_{\perp}/\epsilon_{\parallel})-(\sigma_{\perp}/\sigma_{\parallel})]. \quad (2)$$

κ_1 and η_1 are viscosity coefficients; for PAA $\kappa_1/\eta_1\approx0.3$. A positive ξ favors instability. Equation (1) now can be solved for E_c. Stabilization is found for negative ξ. If the molecular axis is stabilized normal to the walls ($H\parallel E$), k_{33} is replaced by k_{11} while also a different expression for ξ is found.[3] Recently this model has been extended successfully to ac fields.[12,13] In that case the space charges are due to the anisotropic conductivity only and consequently disappear above T_c.

In the theoretical treatments, only instability analysis is given and no predictions are made about the final equilibrium situation. For $\Delta\epsilon<0$ this is a cellular flow pattern; for $\Delta\epsilon>0$ the situation is more complex.[14,15]

III. EXPERIMENTAL RESULTS

In our experiments we used two room temperature nematic liquid crystals with the structure,



The first is a mixture of the two compounds in which R is OCH_3 and R′ is n-C_4H_9 and the reverse[16] (Licrystal N4, Merck AG). The second one is DIBAB,[17] a new room temperature nematic liquid crystal in which both R and R′ are n-C_4H_9 (nematic range 14–28°C). The electric characteristics of N4 and DIBAB are given in Table I. The ξ values are given according to Eq. (2) and using the PAA values for κ_1/η_1. For the relatively small values of $\Delta\epsilon$ involved the second term of Eq. (2) dominates. Consequently the values for ξ are not very different, and the same type of behavior is predicted.

When an electric field is applied perpendicular to the molecular axis in a 10–100-μm layer of N4, domains are seen at about 6 V dc. On increasing the voltage, a gradual change to turbulence is found. The behavior in ac fields and above T_c is also just as summarized above for other compounds with negative $\Delta\epsilon$ such as PAA[5] and N-(p-methoxybenzylidene)-p-n-butylaniline[9] (MBBA).

When an electric field is applied in the same way to DIBAB ($\Delta\epsilon>0$) the result is completely different from N4 ($\Delta\epsilon<0$). At about 7 V (ac or dc) no normal domains are observed, but the molecules switch from the initial orientation perpendicular to the field to an orientation more parallel to the field. This change is gradual as indicated by the change in capacitance of the sample while also at much higher voltages the alignment parallel to E is not complete. Furthermore, at the same threshold usually domains are observed as an irreversible transient effect (ac and dc). At a constant voltage above V_c these domains change into "loop domains"[18,19] that disappear after some time. This decay time becomes shorter for higher voltages while no turbulence and dynamic scattering is observed. We have varied the conductivity (by doping), the electrode materials, and the treatment of the surfaces. The effects were only marginal at best. Similar results as for DIBAB were obtained for nematic dialkyl-substituted azo compounds that have $\Delta\epsilon\approx0.3$.[17]

Especially in dc fields, where injected space charge should be present, the absence of circular flow in DIBAB is somewhat unexpected. Therefore we watched small dust particles in the nematic, which are known to follow the hydrodynamic motion.[7,8] When a dc field is applied to DIBAB above T_c these particles have a circular motion, moving in and out of focus, as for compounds with $\Delta\epsilon<0$. On cooling below T_c this motion disappears and only a reorientation is observed at about the same threshold. Thus the circular hydrodynamic flow due to the injected space charge is counteracted and suppressed in the nematic phase.

IV. DISCUSSION

The difference in behavior between compounds with positive and negative $\Delta\epsilon$ leads to several questions. In principle the change in orientation for compounds with $\Delta\epsilon>0$ could be explained as a purely dielectric effect, analogous to the situation in a magnetic field.[20] Next the question of electrohydrodynamic (in)stability

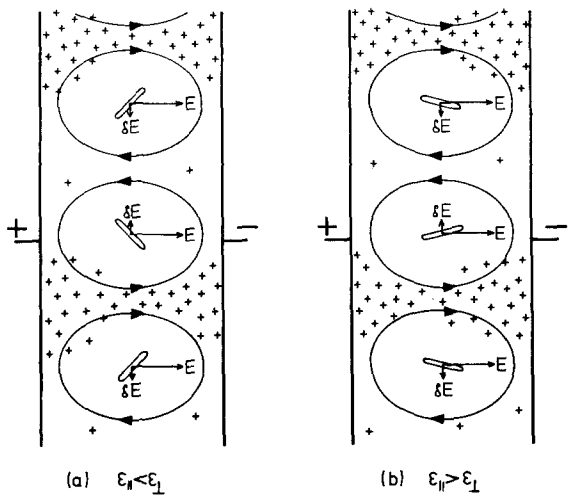


FIG. 1. Orientation in the bulk of the nematic for different sign of $\Delta\epsilon$.

can be considered for the new orientation. If the molecular axis is completely parallel to E then indeed a negative ξ and thus stability is predicted. However, the fact that domains are observed as a transient effect at the same voltage where the reorientation starts, indicates that a distinction between thresholds for dielectric switching and for electrohydrodynamic instability is artificial.[15] The disappearance of the circular flow in dc fields on cooling below T_c is further evidence of this fact. Therefore we shall leave the instability conditions and concentrate on the situation at a later stage once some type of instability is present.

Starting from the Felici model the occurrence of domains above and below T_c in dc fields can, in principle, be understood. However, the theory must be extended to account for the fact that the cellular flow disappears below T_c in the case $\Delta\epsilon>0$ and not for $\Delta\epsilon<0$. This can be done by combining the Felici model with elements of the Carr–Helfrich theory in a somewhat modified form.[21]

If $\Delta\epsilon$ is *negative* the field does not tend to modify the alignment due to the walls. However, in the bulk the flow velocity of the injected charge carriers tends to turn the molecules. In the Felici model the cellular flow pattern is associated with a transverse periodic distribution of the space charge. This leads to extra transverse electric fields δE that support this rotation. Finally an equilibrium is reached in which these two rotating torques are counterbalanced by the dielectric torque of E and the elastic torque [see Fig. 1(a)]. Because $\sigma_{\parallel}>\sigma_{\perp}$ this situation leads to a nonuniform current distribution that tends to *stabilize* the initial space charges. In the dc case this means that the space charges due to injection and due to the anisotropic conductivity add up. In the ac case there is no injection in agreement with the disappearance of the cellular flow above T_c.

If $\Delta\epsilon$ is *positive* the initial situation is still the same. But now in the bulk both the field E and the hydrodynamic torque due to the flow of ions in transit tend to turn the molecules, while only the elastic torque stabilizes. Above the threshold voltage the molecules are more or less parallel to E, and strong hydrodynamic effects are not present any longer. The field effect can dominate and in case of a transverse periodic charge distribution the molecules tend to be parallel to $\mathbf{E}+\delta\mathbf{E}$. This situation is sketched in Fig. 1(b). Now $\sigma_{\parallel}>\sigma_{\perp}$ leads to a nonuniform current distribution that tends to *spread* the space charges evenly. Hence concentrations of injected space charge are counteracted by the anisotropic conductivity which explains qualitatively the disappearance of the cellular flow in DIBAB upon cooling below T_c.

As a consequence of this discussion, it should be possible to bring a compound with negative $\Delta\epsilon$ from the initial situation of Fig. 1(a) to that of 1(b) by a magnetic field H *parallel* to E. This can be considered as an overriding of the dielectric torque by the magnetic torque. MBBA[7] and *p*-azoxyphenetole[19] show normal stable domains in dc or ac electric fields. When a magnetic field $H \parallel E$ is applied these domains do indeed change into loop domains and disappear gradually. The complementary effect should be present in DIBAB.

V. FURTHER EXPERIMENTS

If we look at a 100 μm layer of DIBAB, sandwiched in the usual way between planar electrodes at a voltage above V_c, no domains are seen. When an additional magnetic field of several kilo-oersteds is applied *perpendicular* to E normal stable domains and at higher voltages, turbulence and dynamic scattering are observed. These effects are found both in dc and ac fields. The occurrence of loop domains for $H=0$ is

FIG. 2. Local difference in domain formation in the dielectrically isotropic N4/DIBAB sample at 7 V dc. Upper part, $V_c<7$ V; lower part, $V_c>7$ V.

consistent with these observations in a magnetic field. There is an initial alignment due to the walls that can cause domains on application of an electric field as a irreversible transient effect.

The sum of the dielectric and the magnetic torque determines clearly the form of the instability. Therefore it is interesting to consider a dielectrically isotropic mixture of N4 and DIBAB (see Table I) for $H=0$. Domains are observed at about 7 V dc, while at higher voltages turbulence and dynamic scattering is found. However, here threshold variations of a few volts are observed within one sample (see Fig. 2). The sharp boundary lines between these regions move in time and depend on the history of the sample. Clearly the threshold voltage depends on the orientation of the molecules. This texture effect is even more pronounced in the ac case. At some places no domains are formed at all. On increasing the voltage these places tend to grow over the whole sample, and no general turbulence is observed. This rather ambiguous behavior could be expected as without dielectric or magnetic torque the rather ill-defined wall effects can dominate.

One case of $\Delta\epsilon>0$ has been reported that does not fit in completely with our model: Domains have been observed in *N*-(*p*-methoxybenzylidene)-*p*-aminobenzonitrile[22] (PEBAB) which has $\epsilon_{||}=21$ and $\epsilon_{\perp}=7$.[23] These domains exist in dc fields only, and the cellular flow persists above T_c. That the cellular flow still exists below T_c could be related to the large value of ϵ which gives an increased dissociation into ionic impurities. Then stronger injection is possible due to double layers at the electrodes. This could lead to a situation where the counteracting effects of the anisotropic conductivity are not strong enough to spread the injected space charge.

VI. CONCLUSIONS

Instabilities have been observed for nematics with $\Delta\epsilon>0$ and $\Delta\epsilon<0$ in dc and ac electric fields. For $\Delta\epsilon<0$ the instability is visible as the well-known domain pattern. For $\Delta\epsilon>0$ a reorientation only is observed. The type of instability is determined by the direction of the dielectric torque. A different orientation occurs in the nematic for positive and negative $\Delta\epsilon$, that in turn determines the effect of the anisotropic conductivity on the space charges. This situation and hence the type of instability can be changed by an appropriate magnetic field.

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