Mol. Cryst. Liq. Cryst., Vol. 26, pp. 235-243
© Gordon and Breach Science Publishers, Ltd.
Printed in Dordrecht, Holland

Nematic Phenyl Benzoates in Electric Fields. II. Instabilities Around the Frequency of Dielectric Isotropy†

W. H. de JEU and Th. W. LATHOUWERS

Philips Research Laboratories
Eindhoven
Netherlands

(Received April 19, 1973)

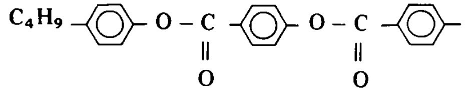
The instabilities in AC fields are discussed for a planar layer of a nematic mixture of two phenyl benzoates. Due to a relaxation of $\epsilon_{\parallel}$ a reversal of the sign of the dielectric anisotropy $\Delta\epsilon$ occurs at the frequency f_0. Above f_0 (negative $\Delta\epsilon$) there is a conduction regime with domains and dynamic scattering. This regime can be understood using an extension of the existing onedimensional model for electrohydrodynamic instabilities in which the dielectric losses of $\epsilon_{\parallel}$ are taken into account. At low frequencies (large positive $\Delta\epsilon$) a Freedericks-transition from a planar to a hometropic orientation occurs. In between is a region (small positive $\Delta\epsilon$) where domains are observed at the threshold and disappear at higher voltages. For this region a two-dimensional model combining the two limiting cases is essential.

INTRODUCTION

In Part I[1] we discussed the static dielectric permittivities and the relaxation of $\epsilon_{\parallel}$ of some nematic phenyl benzonates. In the case of a positive static dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} > 0$) this relaxation leads to a change of sign of $\Delta\epsilon$ at f_0, the frequency of dielectric isotropy. In Part I some compounds and mixtures

† Partly presented at the Fourth International Liquid Crystal Conference, Kent, Ohio, USA, August 21-25, 1972.

were reported where f_0 is quite low (kHz range). In this paper we shall discuss the instabilities in AC-fields around f_0. As typical compound we chose the eutectic mixture of the binary systems


(B1/B2)

with R is C_4H_9 and OCH_3, respectively (nematic range 68–191°C). In Part I this mixture was indicated as B1/B2; the dielectric data were given in Figures 5 and 6. The dielectric properties relevant to this paper are summarized in Table 1. We shall use the complex dielectric permittivity $\epsilon_{\parallel} = \epsilon'_{\parallel} - \epsilon''_{\parallel}$. As the relaxation can be described with a single relaxation time τ_R[1] we have

$$\epsilon'_{\parallel} = (\epsilon_s + \epsilon_\infty \omega^2 \tau_R^2)\,/\,(1 + \omega^2 \tau_R^2), \tag{1a}$$

$$\epsilon''_{\parallel} = (\epsilon_s - \epsilon_\infty)\omega\tau_R\,/\,(1 + \omega^2 \tau_R^2). \tag{1b}$$

ϵ_s is the low-frequency value of $\epsilon_{\parallel}$, ϵ_∞ the high-frequency value (after the relaxation has occurred).

Some preliminary results on instabilities in AC fields in a similar situation were reported earlier.[2] Above f_0 a conduction regime[3] with domains and dynamic scattering is observed. In this paper we shall discuss this frequency region more quantitatively. Then the behaviour at low frequencies (large positive $\Delta\epsilon$) is discussed where the instabilities can be described as a Freedericks-transition from planar to homeotropic. Finally there is an intermediate region (small positive $\Delta\epsilon$) that connects the two limiting cases.

EXPERIMENTAL RESULTS

The instabilities in planar layers of B1/B2 were investigated at various temperatures and conductivities. The samples were placed between crossed polarizers at 45° with the director in a parallel light beam from a He-Ne laser. The trans-

Table 1 Some Dielectric Properties of the B1/B2 Mixture[1]

t(°C)	f_R(kHz)	ϵ_s	ϵ_∞	f_0(kHz)	$\epsilon_\perp$
70	28	9.15	3.45	41	5.46
80	55	8.69	3.45	80	5.32
90	95	8.35	3.45	135	5.25

mitted light was recorded as a function of the slowly increasing voltage over the sample. Above the threshold this gives an interference pattern. With this method the threshold voltage could be determined within 0.2 V. The nature of the instabilities was investigated using a Leitz Ortholux microscope. The quasi-static conductivities were measured at 1592 Hz with a Wayne-Kerr B641 autobalance bridge. As the samples had a planar orientation in fact $\sigma_\perp$ was measured.

At low frequencies (at 70°C for $f < 30$ kHz) a Freedericks-type transition from planar to homeotropic is observed, starting at a voltage threshold varying from 3 tot 6 V. We emphasize that even in heavily doped samples there are no domain-patterns as have been observed for frequencies $\lesssim$ 100 Hz in some compounds with rather small positive values of $\Delta\epsilon$[4,5] The behaviour around f_0 is summarized in Figure 1. Between 33 kHz and f_0 ($\Delta\epsilon < 0.5$) Williams-type domains are observed above a voltage threshold. These domains are stable over a small voltage region while on increasing the voltage further they disappear via loop domains, leaving only the effect of reorientation. (Just as described in Ref. 5 for di-*n*-butyl-azoxybenzene at 50–100 Hz). The voltages where the loop domains have disappeared are indicated by the crosses in Figure 1.

Above f_0 again domains are observed at the voltage threshold V_c. When the voltages is further increased in this region they give way to turbulence and dynamic scattering. With increasing frequency V_c increases too, leading to a

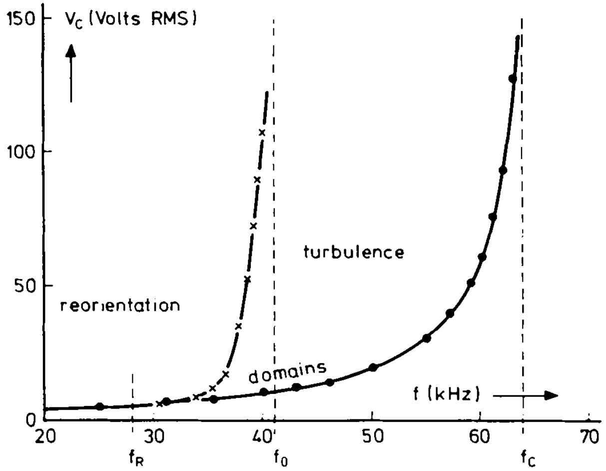


FIGURE 1 Threshold for instability of a planar layer of the B1/B2 mixture around the frequency of dielectric isotropy f_0 (d = 50 μm, $\sigma = 6.10^{-9}$ Ω^{-1}cm^{-1}, $t = 70°$C); crosses (x) indicate the disappearance of the domains.

critical frequency f_c above which chevrons can be observed. The region from f_0 to f_c resembles the conduction regime of a "normal" nematic with $\Delta\epsilon < 0$ at low frequencies. Figure 2 shows the dependence of f_c on the quasi-static conductivity $\sigma_\perp$ for various samples. There appears to be a linear relation between f_c and $\sigma_\perp$ but f_c does not coincide with f_0 in the limit of zero conductivity.

DISCUSSION

Negative dielectric anisotropy ($f > f_0$)

The existence of electrohydrodynamic instabilities at high frequencies is consistent with an extension of the theoretical model of Dubois-Violette *et al.*[6] in which the dielectric losses of $\epsilon_\parallel$ are taken into account. In this model a nematic is considered under influence of an electric field $E = E_M \cos \omega t$ (in the Z-direction) perpendicular to the director (X-dirextion). The model is one-dimensional as only perturbations of the director along X are considered: $n = n(x)$. The boundary conditions are afterwards accounted for approximately by taking $k = \pi/d$; k is the wave vector of the perturbation and d the thickness of the sample. In a linear approximation hydrodynamic (in)stability is governed by two coupled equations. One for the local curvature of the molecular alignment ψ (from the balance of torques), the other for the charge density q (from the

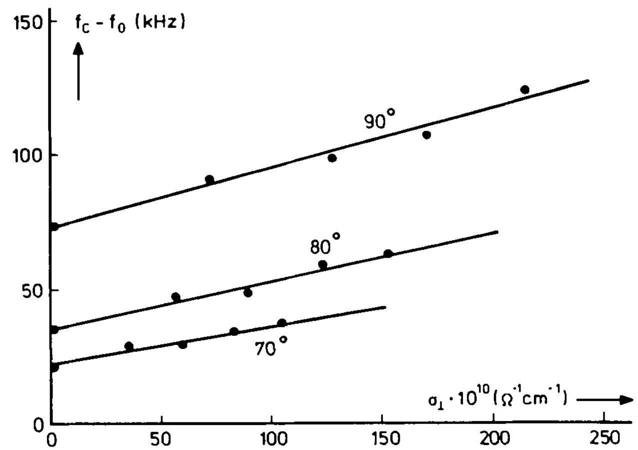


FIGURE 2 Dependence of the width of the conduction regime on the conductivity (B1/B2 mixture).

continuity equation for charges). Assuming a *static* ψ this leads to the well-known formula for the threshold in the conduction regime[6]:

$$\overline{E_c^2} = \frac{1+\omega^2\tau^2}{\Delta\epsilon\omega^2\tau^2+\Theta_H}\;\frac{4\pi\epsilon_\parallel}{\epsilon_\perp}\;k^2K_{33}. \tag{2}$$

$\tau = \epsilon_\parallel/4\pi\sigma_\parallel$ is the relaxation time for the space charge, K_{33} the elastic constant for bend, Θ_H a parameter characteristic of the material depending on dielectric constants, conductivities and viscosity coefficients. (Θ_H is positive and of the order of 1.)

For negative $\Delta\epsilon$ the conduction regime is limited by the zero of the denominator in Eq. (2):

$$\omega_c = \sqrt{\Theta_H/\Delta\epsilon}.\;4\pi\sigma_\parallel/\epsilon_\parallel. \tag{3}$$

The change of sign of $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ can be accounted for by substituting Eq. (1a) into Eq. (2). This already leads to a conduction regime above f_0 with a critical frequency f_c. However the width $f_c - f_0$ is very small and not proportional to the conductivity.

Goossens[7] has extended the derivation of the coupled equations for ψ and q taking into account the complex nature of $\epsilon_\parallel = \epsilon_\parallel' - i\epsilon_\parallel''$. Again assuming a static ψ this leads to a threshold:

$$\overline{E_c^2} = \frac{1+(\omega\tilde{\tau}+\epsilon_\parallel''/\epsilon_\parallel')^2}{\widetilde{\Delta\epsilon}\,(\epsilon_\parallel'/\epsilon_\parallel)^2\,(\omega\tilde{\tau}+\epsilon_\parallel''/\epsilon_\parallel')^2+\epsilon_\parallel''\tilde{\tilde{\delta}}\,(\omega\tilde{\tau}+\epsilon_\parallel''/\epsilon_\parallel')+\tilde{\Theta}_H}\;\frac{4\pi\epsilon_\parallel'}{\epsilon_\perp}\;k^2K_{33} \tag{4}$$

where $\epsilon_\parallel^2 = (\epsilon_\parallel')^2 + (\epsilon_\parallel'')^2$, $\widetilde{\Delta\epsilon} = \epsilon_\parallel^2/\epsilon_\parallel' - \epsilon_\perp$, $\tilde{\tau} = \epsilon_\parallel^2/4\pi\epsilon_\parallel'\sigma_\parallel$,

$\tilde{\tilde{\delta}} = (\tilde{\delta} + \tilde{\sigma}_H\tilde{\tau}\epsilon_\parallel'/\epsilon_\parallel^2)$ with

$\tilde{\sigma}_H = \sigma_\parallel(\epsilon_\perp\epsilon_\parallel'/\epsilon_\parallel^2 - \sigma_\perp/\sigma_\parallel)$ and $\tilde{\delta} = (\eta''/\eta')(\gamma_1 - \gamma_2)/2\gamma_1 - \widetilde{\Delta\epsilon}\epsilon_\parallel'/\epsilon_\parallel$,

and finally $\tilde{\Theta}_H = (\epsilon_\parallel' - \epsilon_\perp) + \delta\sigma_H\tau\epsilon_\parallel'/\epsilon_\perp$.

All the quantities with tilde reduce to the corresponding normal quantities given in Ref. 6 for $\epsilon_\parallel'' \rightarrow 0$. Then Eq. (4) also reduces to Eq. (2). The most significant difference from Eq. (2) is the occurance in the denominator of a term proportional to $\epsilon_\parallel''$ that is *linear* in $\omega\tilde{\tau}$. The critical frequency ω_c is determined by the zero of the denominator of Eq. (4) with $\epsilon_\parallel'$ and $\epsilon_\parallel''$ given by Eqs. (1a) and (1b).

This leads to a form in ω of the sixth degree. An approximate solution can be obtained using

$$\tau_R \ll \tau \quad \text{and} \quad \omega\tau_R \approx 1 \tag{5}$$

As for the conductivities used $\tau^{-1} \leqslant 5$ kHz the first approximation is fully justified. The second one is only true if both f_c and f_0 are rather close to f_R. We then find appoximately

$$\omega_c = \frac{\sqrt{\alpha/\beta}}{\tau_R} + \frac{(\epsilon_s - \epsilon_\infty)\tilde{\tilde{\delta}}}{2\sqrt{\alpha\beta}}\cdot\frac{1}{\tau} \tag{6}$$

with $\alpha = 1 - \epsilon_\perp/\epsilon_s$ and $\beta = \epsilon_\perp\epsilon_\infty(1 - \epsilon_\infty/\epsilon_s)/\epsilon_s^2$.

According to Eq. (6) the critical frequency is proportional to τ^{-1} or $\sigma_\parallel$. Assuming that the ratio $\sigma_\parallel/\sigma_\perp$ is constant this is in agreement with the experimental results of Figure 2. The value of ω_c in the limit of zero conductivity can easily be calculated using the data of Table 1. At 70, 80 and 90°C we find for $f_c - f_0$ respectively 6, 9 and 13 kHz which compares with experimental values of 23, 35 and 37 kHz. The trend is well reproduced; that the quantitative agreement is not better can be attributed to the second approximation (Eq. (5)).

At first sight one might be somewhat surprised at the existance of hydrodynamic instabilities at frequencies far above τ^{-1}. However, $\epsilon''\omega$ is equivalent to a normal conductivity. Due to the anisotropy in the losses (experimentally $\epsilon_\parallel''/\epsilon_\perp'' \sim 50$) then space charge is generated. This space charge is in the usual way coupled to the curvature leading to Eq. (4). Of course, τ is not a relaxation time for space charge formed in this way.

Positive dielectric anisotropy ($f > f_0$)

The reorientation in the region below 30 kHz can be described as a Freedericks-transition from planar to homeotropic. Then again a one-dimensional model can be used, but now in the Z-direction: $n = n(z)$. Analogous to the magnetic case[8] this leads to

$$V_c' = \pi\sqrt{4\pi K_{11}/\Delta\epsilon}. \tag{7}$$

The variation of $\Delta\epsilon$ with frequency provides an elegant check on this formula. A logarithmic plot of V_c against $\Delta\epsilon$ indeed gives a straight line at a slope of –0.5 (Figure 3).

The region of small positive $\Delta\epsilon$ between 30 kHz and f_0 forms a transition between the two limiting cases that can be described by a one-dimensional

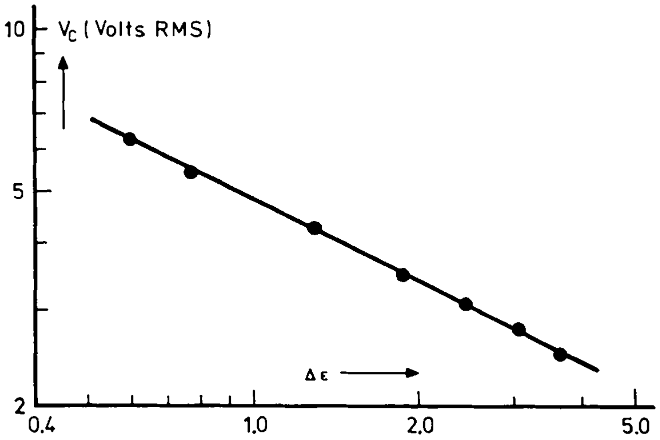


FIGURE 3 Threshold voltage versus dielectric anisotropy for frequencies up to 30 kHz (B1/B2 mixture from Figure 1).

model in the Z- and X-direction, respectively. As argued before[5] a two-dimensional model is then essential: $n = n(x,z)$. Such a model, although without frequency-dependence, has been reported;[9] results for a planar nematic with positive $\Delta\epsilon$ were given recently.[10] For values of $\epsilon_\parallel/\epsilon_\perp < 1.05$ at the threshold V_c domains are predicted (period of the distortion of the order of thickness). In addition on increasing the voltage the spatial period increases too until at V_c' the Freedericks-transition is reached (period of the distortion infinity). Although in a strict sense the linear approximation used in the model is only valid at the threshold, it is tempting to identify the voltage region $\Delta V = V_c' - V_c$ with the region of existence of the domains as found experimentally.

Using the above idea the theoretical value of $\epsilon_\parallel/\epsilon_\perp = 1.05$ where V_c' becomes different from V_c agrees very well with the results of Figure 1. Furthermore ΔV does indeed increase when $\epsilon_\parallel$ becomes closer to $\epsilon_\perp$. On the other hand the voltage of disappearance of the last hydrodynamic instabilities (loop domains) as given in Figure 1 is appreciably higher than the voltage V_c' where the Freedericks-transition can be expected. Experimentally the period of the domains is rather constant in the region from V_c to V_c'. It is only when V_c' is reached that the period increases because loop domains are formed that gradually disappear.

Qualitively the instabilities for small positive $\Delta\epsilon$ can be understood from an extrapolation of the two linearized one-dimensional models. Assuming a small perturbation the question of hydrodynamic instability is governed by the balance of the stabilizing dielectric and elastic torque and the destabilizing shear torque due to the space charge induced by the anisotropic conductivity or losses.

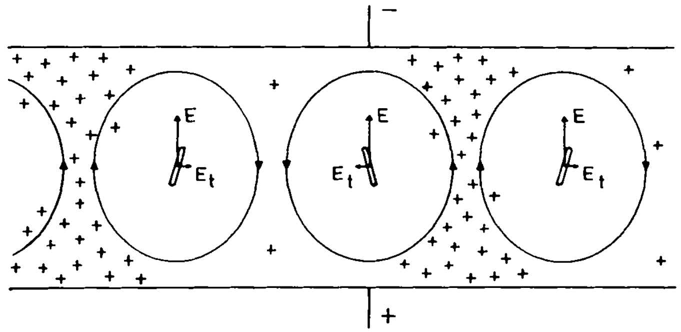


FIGURE 4 Spreading of the space charge due to the reorientation at higher voltages for small positive $\Delta\epsilon$.[11]

For very small values of $\Delta\epsilon$ the dielectric torque can be neglected. This explains why the same type of domain patterns are found around f_0 for $\Delta\epsilon > 0$ and $\Delta\epsilon > 0$. For $\Delta\epsilon > 0$ on the other hand, at voltages above the extrapolated threshold for the Freedericks transition V_c' a further reorientation occurs. Then the space charge does not increase strongly anymore, and finally at an angle θ_0 for which $tg^2\ \theta_0 = \sigma_\parallel/\sigma_\perp$ the anisotropy in the conductivity is effectively zero. At angles larger than θ_0 we get a non-uniform current distribution that tends to spread the space charge concentrations associated with the domain pattern. This situation is sketched in Figure 4[11] and explains qualitatively the disappearence of the domains. It is clear that for large positive $\Delta\epsilon$ where $V_c' < V_c$ the domains cannot be formed at all.

Acknowledgements

The authors thank Dr. W. J. A. Goossens for valuable discussions on the hydrodynamic instabilities and Dr. R. Steinsträsser (E. Merck) for making the phenyl benzoates available to us.

References

1. de Jeu, W. H. and Lathouwers, Th. W., *Mol. Cryst. and Liq. Cryst.* 26, 225 (1974), preceding paper.
2. de Jeu, W. H., Gerritsma, C. J., van Zanten, P. and Goossens, W. J. A., *Phys. Lett.* 39A, 355 (1972).
3. Orsay Liquid Crystal Group, *Mol. Cryst. and Liq. Cryst.* 12, 251 (1971).
4. Gruler, H. and Meier, G., *Mol. Cryst. and Liq. Cryst.* 12, 289 (1971).
5. de Jeu, W. H., Gerritsma, C. J. and Lathouwers, Th. W., *Chem. Phys. Lett.* 14, 503 (1972).

6. Dubois-Violette, E., de Gennes, P. G. and Parodi, O., *J. Phys. (Paris)*, **32**, 305 (1971).
7. Goossens, W. J. A., *Phys. Lett.* **40A**, 95 (1972).
8. Saupe, A., *Z. Naturf.* **15a**, 815 (1960).
9. Penz, P. A. and Ford, G. W., *Phys Rev.* **A6**, 414 (1972).
10. Penz, P. A., Mol. Cryst. and Liq. Cryst. **23**, 1 (1973).
11. de Jeu, W. H. and Gerritsma, C.J., *J. Chem. Phys.* **56**, 4752 (1972).