

CHAPTER VII

ELECTROHYDRODYNAMIC INSTABILITIES IN NEMATICS HAVING NEGATIVE CONDUCTIVITY ANISOTROPY AND POSITIVE DIELECTRIC ANISOTROPY

7.1 Introduction

The anisotropies in the dielectric constant and the electrical conductivity of nematic liquid crystals give rise to many interesting electrohydrodynamic phenomena. It was observed by Kast, as early as 1931, that the molecular alignment in p-azoxyanisole under a high frequency electric field is different from that under a low frequency electric field. Zvetkoff and Mikhailov (1938) suggested that the anomalous alignment observed under the action of the low frequency electric field might be due to the anisotropy in the electrical conductivity of liquid crystals. Carr (1963) made a systematic study of the anomalous alignment in liquid crystals under low frequency electric fields and concluded that it is associated with their conductivity anisotropy.

A pure nematic liquid crystal is a good electrical insulator. However, ionic impurities can be added to make it conducting. Usually, the conductivity anisotropy of such doped samples is positive (i.e., $\sigma_{||} > \sigma_{\perp}$, where $\sigma_{||}$ is the conductivity measured parallel to the director and $\sigma_{\perp}$ that measured in a perpendicular direction): it is easier for the ions to move along $\vec{n}$ rather than perpendicular to it.

this gives rise to the anomalous alignment of the molecules (Carr 1963). Based on these ideas, Helfrich (1969) gave a theory for the electrohydrodynamic instabilities produced by a DC field.

Let us consider a homogeneously aligned sample of a nematic liquid crystal subjected to an electric field $\vec{E}$ (Figure 7.1). The local director in the sample will not be exactly normal to $\vec{E}$, but will be fluctuating about a mean direction, as shown in an exaggerated form in figure 7.2. As a result of the positive conductivity anisotropy of the medium, space charges of opposite signs are formed at the crests and troughs of the bend type fluctuations. While the torques due to the dielectric anisotropy and elasticity tend to stabilise the orientation of $\vec{n}$, the transverse electric field due to the space charges tends to distort it. At the same time the space charges will be set in motion by the applied electric field $\vec{E}$. This, in turn, will produce a spatially varying velocity field. The viscous torque produced by the velocity field will tend to enhance the distortion. At low voltages, the stabilising torques predominate. But, beyond a threshold voltage the destabilising torques will have an upper hand and this results in the electrohydrodynamic instabilities. These are the basic ideas of Helfrich's theory.

This theory was extended to time-dependent phenomena by Dubois-Violette et al (1971). They wrote down the basic

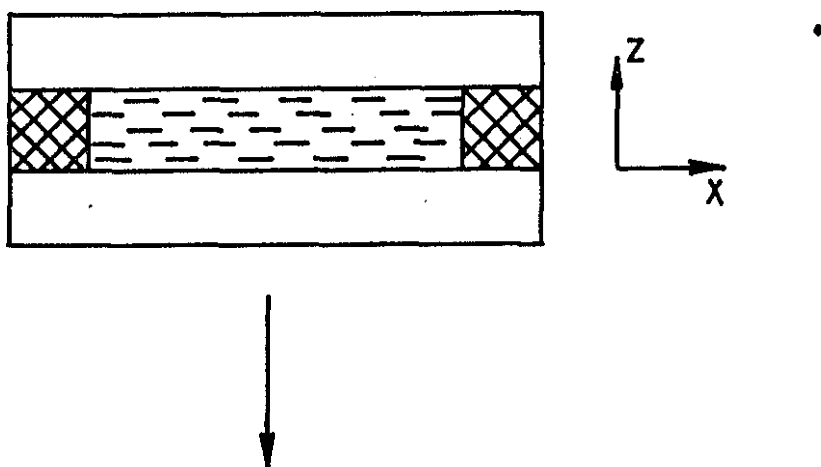


FIGURE 7.1

The sandwich geometry with a homogeneously aligned crystal for observing electrohydrodynamic instabilities in samples with positive ϵ_a and negative $\Delta\epsilon$. The electric field is applied along the a direction. The arrow shows the direction of observation.

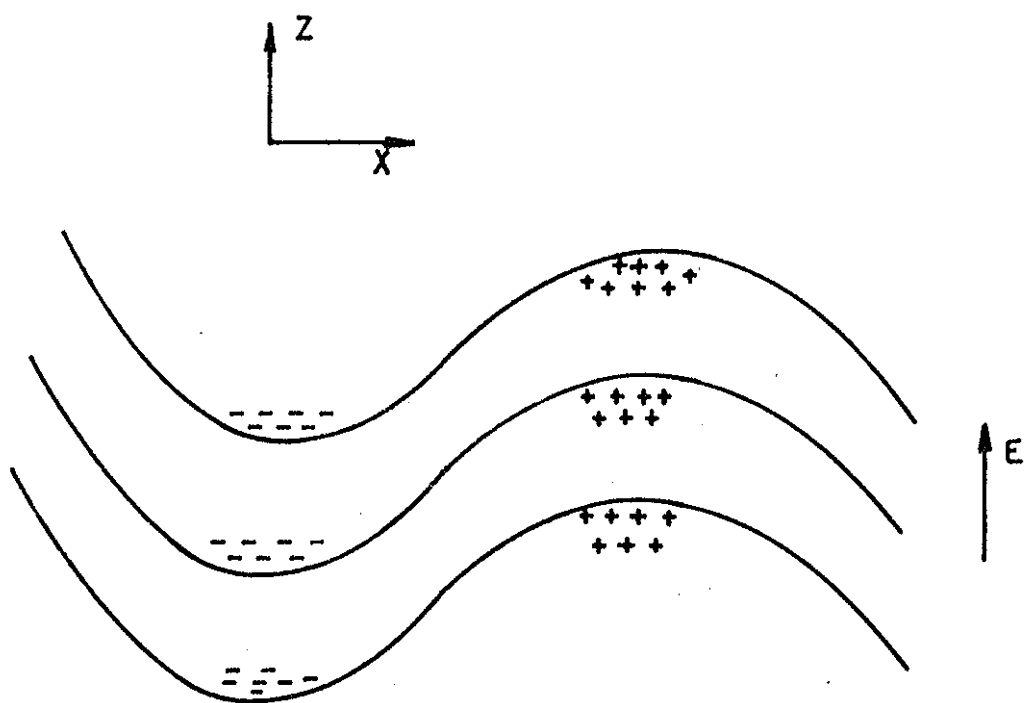


FIGURE 7.2

Bend fluctuations in a sample with negative $\Delta\epsilon$ and positive $\Delta\sigma$ giving rise to space charges under the action of an electric field.

equations for the problem and discussed the solutions in a general way. We shall give a brief description of this theory.

If ϕ is the angle made by the local director with reference to its undistorted orientation and $\gamma = \partial\phi/\partial x$ is the bend curvature, the damping time τ of the bend mode in the presence of the electric field is given by (Dubois-Violette et al 1971, Durand 1976)

$$\frac{1}{\tau} = \frac{[k_{33} k^2 - \frac{\Delta\epsilon \epsilon_{\perp}}{4\pi \epsilon_{\parallel}} E^2]}{\eta_B} = \lambda (E'^2 + E^2) \quad (\text{say}) \quad (7.1)$$

where k_{33} is the bend elastic constant, k is the wave vector of the instability, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the dielectric constants parallel and perpendicular to $\vec{n}$ respectively, $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, and η_B is the 'bend viscosity' coefficient.

The time dependence of ψ and q were derived for small amplitude fluctuations by Dubois-Violette et al (1971). They have written three equations to describe the balance of torque on the director, the balance of charges and the hydrodynamic motion. After eliminating velocity (Durand, 1976) two coupled equations in ψ and q are obtained

$$\dot{\psi} + \frac{\psi}{\tau} + \frac{Eq}{\eta} = 0 \quad (7.2a)$$

$$\dot{q} + \frac{q}{\tau} + \sigma_H \psi E = 0 \quad (7.2b)$$

where τ is the dielectric relaxation time along $\vec{n}$. ($\frac{1}{\tau} = \frac{4\pi \sigma_{\parallel}}{\epsilon_{\parallel}}$),

η is a coefficient of viscosity ($\eta > 0$) and

$$\sigma_H = \sigma_{||} \left(\frac{\epsilon_{\perp}}{\epsilon_{||}} - \frac{\sigma_{\perp}}{\sigma_{||}} \right) \quad (7.3)$$

The two coupled first order differential equations describe the time evolution of the space charge and curvature for any applied electric field.

The equation (7.2b) called the charge equation contains a source term. This term vanishes if $\frac{\sigma_{\perp}}{\sigma_{||}} = \frac{\epsilon_{\perp}}{\epsilon_{||}}$. For the materials with positive conductivity anisotropy and negative dielectric anisotropy, the source term has a positive value.

The equation (7.2a) called the curvature equation also contains a source term. This source term arises from two effects - (a) the induced space charges are dragged along the field producing a shear flow, and (b) the actual field which is the resultant of the applied field and the field due to space charges is tilted with respect to the applied field. Both these are destabilising effects.

The DC threshold voltage is obtained by putting $\dot{\psi} = \dot{q} = 0$. Then equations (7.2a) and (7.2b) reduce to

$$\frac{\psi}{\tau} + \frac{Eq}{\eta} = 0$$

and

$$\frac{q}{\tau} + \sigma_H E \psi = 0.$$

Solving these equations, the threshold value is obtained

$$E_{th}^2 = \frac{E'^2}{\xi - 1} = \frac{k_{33}^2 k^2}{\lambda \eta_B} \frac{1}{\xi - 1}$$

where $\xi = \frac{2}{\eta \lambda}$ is called the Helfrich gain parameter.

Helfrich (1969) has pointed out that due to geometrical constraints, the wave vector k takes an optimum value $\approx \frac{\pi}{d}$. Substituting $k = \frac{\pi}{d}$, we get ,

$$V_{th}^2 = (E_{th} d)^2 = \frac{\pi^2 k_{33}^2}{\lambda \eta_B} \frac{1}{\xi - 1} \quad (7.4)$$

This is the expression for the DC voltage threshold of electrohydrodynamic instabilities.

From this equation it is evident that the instabilities can occur only if $\xi > 1$.

In terms of principal dielectric constants and conductivities the Helfrich parameter can be written as

$$\xi^2 = \frac{\epsilon_{||}^2}{(-\Delta\epsilon) \epsilon_{\perp}} \frac{\eta_B}{\eta} \left(\frac{\epsilon_{\perp}}{\epsilon_{||}} - \frac{\sigma_{\perp}}{\sigma_{||}} \right) \quad (7.5)$$

It is clear from this expression that ξ^2 depends only on ratios of the principal dielectric constants and conductivities and not on their absolute values.

In the case of AC electric fields, at low frequencies

the space charges have sufficient time to relax to the equilibrium zero value and to build up with the opposite sign as the electric field is reversed, the curvature remaining unchanged. In such a case, the destabilizing torques also remain unchanged and a quasi-static distortion can be amplified. This is called the conduction regime, because it is characterised by space charge oscillations in time. At high frequencies, on the other hand, the space charge has no time to relax. In such a case, the instability occurs due to the rapid changes in the sign of the bend curvature γ , which oscillates with the frequency of the applied voltage. This corresponds to the 'dielectric regime' of electrohydrodynamic instabilities. Thus, in the conduction regime q oscillates and γ is static whereas in the dielectric regime γ oscillates and q is static.

Under low frequency AC electric field, i.e., in the conduction regime, solving equations (7.2a) and (7.2b), one gets an expression for threshold field:

$$E_{th}^2 = \frac{k_{33} k^2}{\lambda} \frac{1 + w^2 \tau^2}{\epsilon^2 - 1 - w^2 \tau^2} \quad (7.6)$$

where w is the frequency of the applied field.

We find a voltage threshold since $k \approx \pi/d$ and hence

$$V_{th}^2 = (E_{th} d)^2 = \frac{k_{33} \pi^2}{\lambda} \frac{1 + w^2 \tau^2}{\epsilon^2 - 1 - w^2 \tau^2}$$

When the periodicity of the distortions along the x-direction is comparable to the sample thickness, the distortion cannot be really regarded as pure bend. In addition to the bend, it has a non-negligible splay component due to the variation of ψ in the z-direction. Smith et al (1975) have shown that in such a case the effect of splay distortion can be taken into account by a renormalisation of the elastic constant

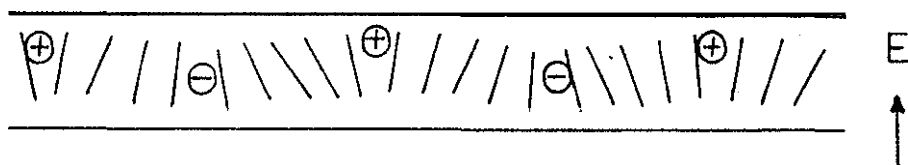
$$k_{33} \rightarrow k_{33} + k_{11} \left(\frac{k_z}{k_x} \right)^2 \quad (7.7)$$

Durand (1976) has suggested that an electrohydrodynamic phenomenon similar to the one observed in nematic liquid crystals of positive $\Delta\sigma$ and negative $\Delta\epsilon$ is, in principle, possible in materials having the reverse characteristics, viz., negative $\Delta\sigma$ and positive $\Delta\epsilon$. However, in the latter case the instability is expected to appear as a splay mode as indicated in figure 7.3 (in a homeotropically aligned sample) rather than as a bend mode,

An approximate description of the electrohydrodynamic instabilities that appear in materials with negative $\Delta\sigma$ and positive $\Delta\epsilon$ is obtained by writing k_{11} instead of k_{33} and interchanging $\parallel$ and $\perp$ in the indices of ϵ and σ in equations 7.3 and 7.4. Then, we get,

$$\sigma_H = \sigma_{\perp} \left(\frac{\epsilon_{\parallel}}{\epsilon_{\perp}} - \frac{\sigma_{\parallel}}{\sigma_{\perp}} \right) \quad (7.8)$$

σ_H is positive as $\epsilon_{\parallel} > \epsilon_{\perp}$ and $\sigma_{\parallel} < \sigma_{\perp}$.



FIG

FIGURE 7.3

Splay fluctuations in a sample **with** positive $\Delta\epsilon$ and negative $\Delta\alpha$ giving rise to space charges under the action of an electric field.

As in the case of materials with positive $\Delta\sigma$ and negative $\Delta\epsilon$, the distortion is a combination of splay and bend in the present case also. To account for the complex distortion, the elastic constant has to be renormalised as follows

$$k_{11} \longrightarrow k_{11} + k_{33} (k_z/k_x)^2 \quad (7.9)$$

where the external electric field is assumed to be acting along the z-axis.

We have seen in chapter V that HOAB exhibits nematic and smectic C mesophases. The conductivity anisotropy of HOAB is negative in the smectic C phase and it remains to be so over a small temperature range above the smectic-nematic transition point (Rondelez 1972). The dielectric anisotropy of HOAB is negative. On the other hand, liquid crystals having cyano end groups have large positive dielectric anisotropies, but very small conductivity anisotropies (Mircea-Roussel et al 1975). When such cyano compounds are added to HOAB, the binary mixtures show induced smectic mesomorphism (see, chapter V). It is expected that at temperatures immediately above the smectic-nematic transition point of some of these mixtures, $\Delta\sigma$ will be negative and $\Delta\epsilon$ will be positive. In the following, we describe the electrohydrodynamic flow patterns seen in such mixtures.

7.2 Experimental

The sample holder. The sample holder (figure 7.4a) is a cylindrical block of copper containing a rectangular slot in one of its flat faces. The sample cell consisting of two transparent, conducting glass plates $\textcircled{C}$ separated by nylon spacers $\textcircled{F}$ is placed in this slot. This is held in position by means of another cylindrical copper block which can be fixed to the first one with the help of screws. The electrical contact to the electrodes is provided by two stainless steel screws $\textcircled{A}$ which are properly insulated from the copper blocks. The tip of one of the screws presses directly against the conducting side of one of the glass plates. The tip of the other screw makes electrical contact with the conducting surface of the other glass plate through a copper plate $\textcircled{B}$ (which is insulated from the copper blocks) and a button $\textcircled{D}$ of conducting rubber. Optical observations were made through a hole (~ 10 mm in diameter) present along the axis of the sample holder. The sample holder is placed inside a suitable oven.

Temperature control and measurement. The oven was heated using direct current from a stabilised power supply. Before making any observation or measurement sufficient time (~ 30 min.) was allowed so that the sample attained a steady temperature. The temperature was measured using a calibrated chromel-alumel thermocouple and a multimeter (APLAB Model 1005).

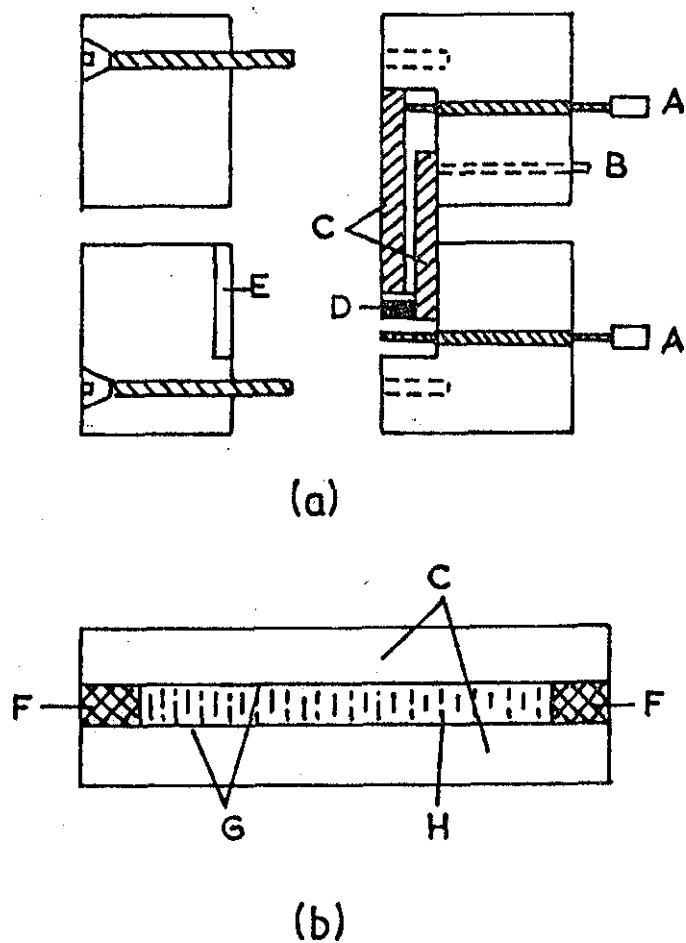


FIGURE 7.4

- (a) Schematic diagram of the sample holder used in the study of electrohydrodynamic instabilities.
- (b) The liquid crystal cell in the sandwich geometry with a homeotropically aligned sample.

Sample preparation. The electrohydrodynamic phenomena were studied in three mixtures, viz., (a) a mixture of HOAB and 7CE (molar ratio $\approx 85 : 15$); (b) a mixture of HOAB and 10 OMCP (molar ratio $\approx 90 : 10$); and (c) a mixture of HOAB and 2 OMCP (molar ratio $94 : 6$). All these mixtures exhibit the phenomenon of induced smectic mesomorphism.

The experiments were performed using the conventional sandwich geometry (Figure 7.4b). The thickness of the cell was in the range 12μ to 25μ .

Homeotropic alignment of the sample was achieved by treating the glass plates with octyl trimethyl ammonium bromide (OTAB). The sample was injected in the nematic phase into the space between the glass plates using a capillary tube.

The AC voltage was supplied by an R.C. oscillator (Orion type 1113/E) and was measured using an AC microvoltmeter (Systronics type 411). The electrohydrodynamic instability patterns were observed in sodium light through a polarising microscope. The patterns were photographed using an electronic flash.

7.4 Observations

We shall describe the patterns observed in a typical sample of thickness $\sim 20 \mu$. The sample was cooled to the required temperature from the isotropic phase. At temperatures

slightly lower than the nematic-isotropic **transition** point no instability patterns were seen even **at** voltages as **high** as 250 V. The instability patterns were seen only **below** a certain temperature **in** the **nematic** phase and could be seen right down to the **AI** transition point.

At **any** temperature in **this** range, **as** the applied voltage is slowly **increased**, the instability **pattern begins** to appear at a **threshold** voltage. **To** begin with, the pattern **is** in the **form** of a few crosses (figure 7.5a). At the threshold we could see odd-shaped dust **particles executing** circular motion in both **clockwise** and **anticlockwise** directions. At a voltage **slightly** above the threshold, the whole field of view **is seen to be** covered by **instabilities** and a **finger** print texture **is** obtained (Figure 7.5b). **In this** pattern, the **circular** symmetry **could** be seen clearly **around** a few points. **As** the voltage is further **increased**, a **cross-hatched** pattern **is** seen (Figure 7.5c). At **high frequencies** (> 6000 Hz), a **honeycomb-like** texture (figure 7.5d) is seen at voltages of the order of 100 V. Above roughly **twice** the threshold voltage, rigorous movement of the fluid accompanied by **dynamic scattering** is **observed**. At low frequencies, the spatial periodicity of the pattern is found to be comparable, to the sample **thickness**. **In** some cases, it is found to be somewhat **higher than the** sample thickness. **As** the **frequency** is increased, this periodicity is found to **decrease** gradually.

The frequency dependence of the threshold voltage is shown

FIGURE 7.5

**Electrohydrodynamic patterns in a mixture of XOAB
and 2 OMOPC (molar ratio 94 : 6) Crossed polars
(x 100)**

$$\sigma \approx 2 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$$

- (a) at 20 Hz and 22 V (96°C)**
- (b) at 2000 Hz and 35 V (100°C)**
- (c) at 20 Hz and 29 V (96°C)**
- (d) at 6000 Hz and 110 V. (100°C)**

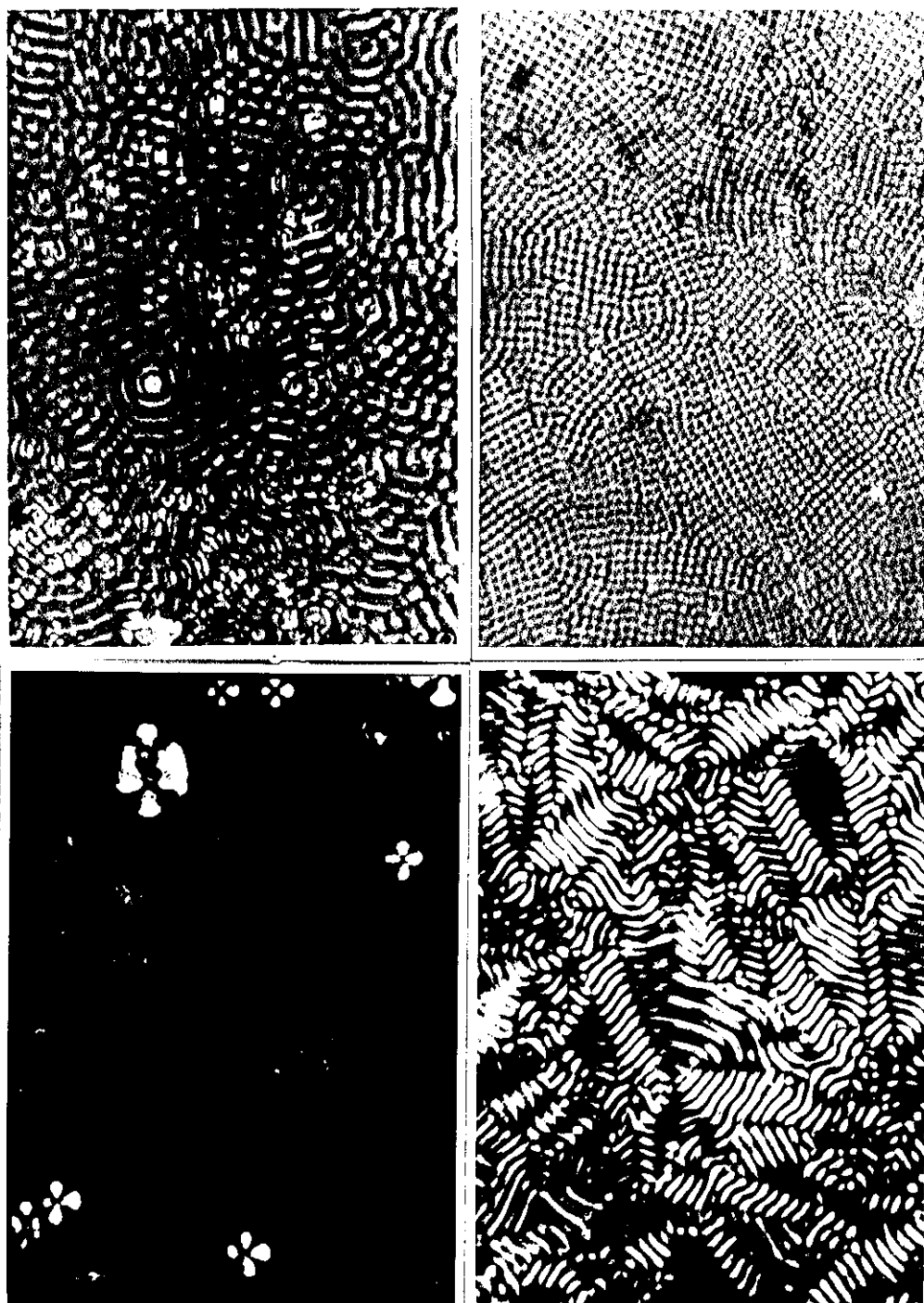


FIGURE 7.5

in figure 7.6. The curves obtained here resemble the curves got in the conduction regime of nematics having negative $\Delta\epsilon$ and positive $\Delta\sigma$. Probably at high enough frequencies one may get the counterpart of the dielectric regime. But we could not apply high frequency electric fields due to the non-availability of suitable voltage sources.

In figure 7.7, the temperature dependence of the threshold voltage is shown. As the temperature is increased from the smectic-nematic transition point, the threshold voltage decreases, attains almost a flat minimum and thereafter increases. Above a certain temperature no instability was observed even at the highest available voltage (250 V).

7.4 Discussion

As mentioned in chapter V, HOAB shows smectic C and nematic mesophases. Rondelez (1972) measured the electrical conductivity of HOAB in both these phases. He observed that the conductivity anisotropy of HOAB is negative in the smectic C phase and depending on the dopant and its concentration, it remains negative over a fairly large temperature range above the smectic-nematic transition point. Close to the NI transition point $\Delta\sigma$ becomes positive. The dielectric anisotropy of HOAB is negative throughout the nematic phase. The samples used by us are binary mixtures of HOAB and small quantities of cyano compounds like 7CB, 10 OMCP or 2 OMCP which have large

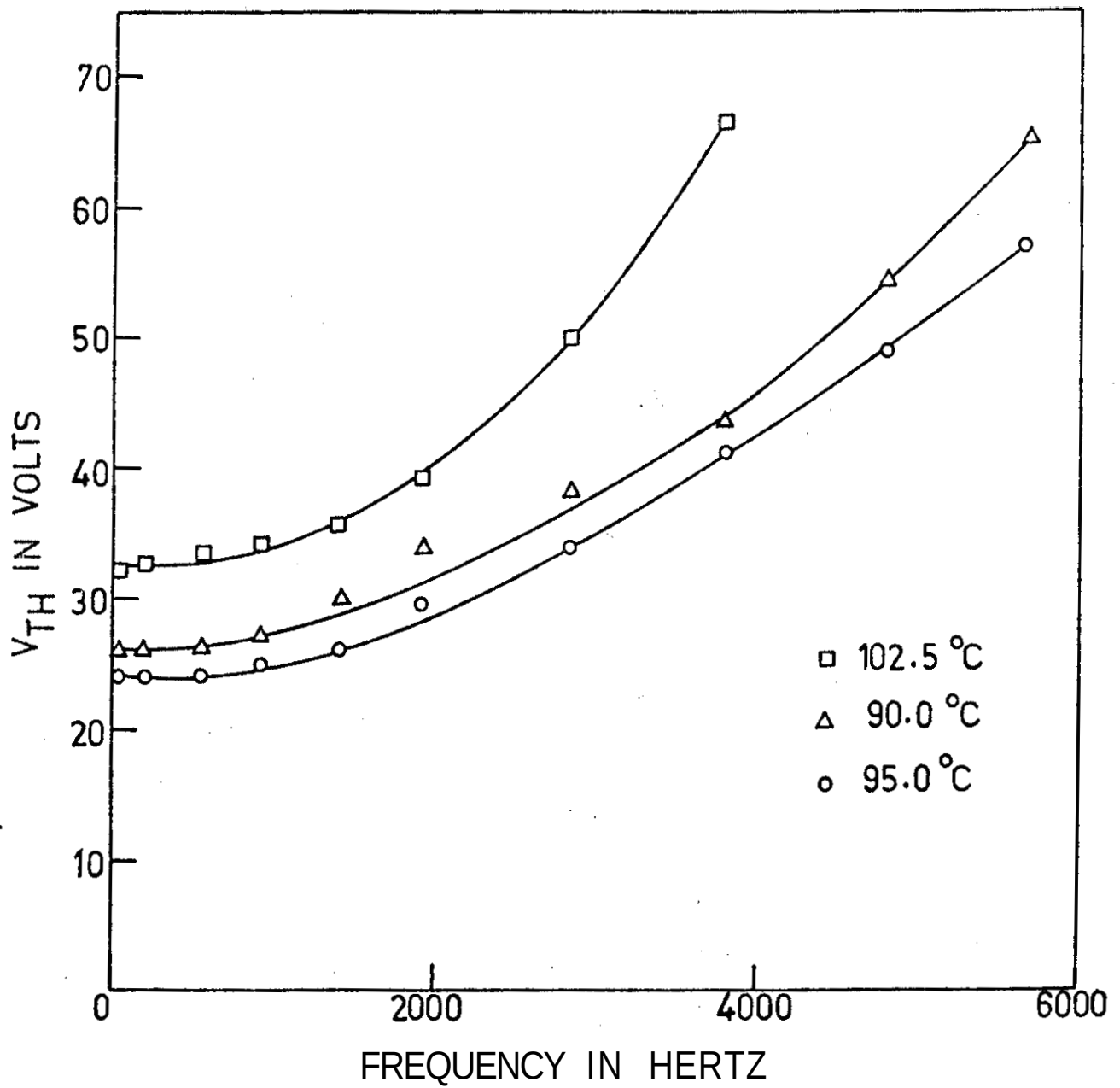


FIG.

FIGURE 7.6

Frequency dependence of the threshold voltage of electrohydrodynamic instabilities at three different temperatures. The sample used was the same as that described in figure 7.5.

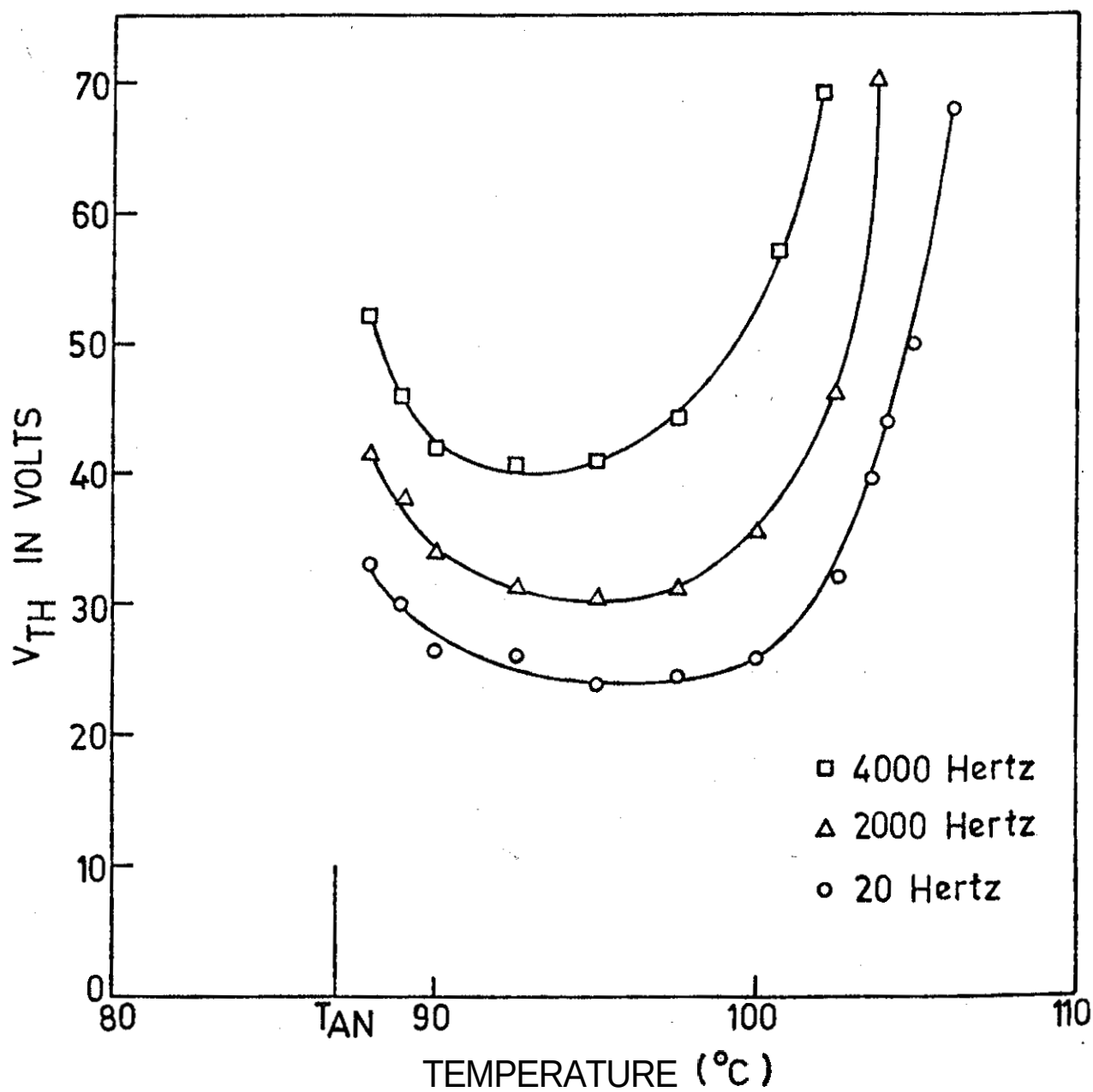


FIGURE 7.7.

Temperature dependence of threshold voltages of electrohydrodynamic instabilities at three different frequencies. The sample used was the same as that described in fig. 7.5.

positive $\Delta\epsilon$ (Ratna and Shashidhar 1977). We have observed that in these mixtures, ~~that~~ at temperatures close to the NI transition point (where no electrohydrodynamic instabilities were seen) the homeotropic alignment improved on applying the electric field. This confirms that the dielectric anisotropy of the medium is positive.

Before discussing a possible explanation for the patterns observed by us, we will review some earlier observations made by others.

Goscianski and Leger (1975) have observed some electrohydrodynamic patterns above the smectic-nematic transition point of 4,4'-di-octyloxyazoxybenzene, a higher homologue of EOAB. For octyloxyazoxybenzene both $A\sigma$ and $\Delta\epsilon$ are negative in the nematic phase. Goscianski and Leger have reported that for this compound the threshold voltage is high near the nematic-smectic transition point and as the temperature is increased, the threshold voltage decreases monotonically. They have concluded that close to the nematic smectic transition point the Helfrich parameter $\xi^2 < 1$ and have attributed the instabilities seen in this range to twist fluctuations in the sample.

Blinov et al (1979) have also made studies on the instability patterns observed in some pure compounds and mixtures above the NI transition points. They have studied systems having negative $\Delta\sigma$ and negative $\Delta\epsilon$ as well as those having negative

$\Delta\sigma$ and positive $\Delta\epsilon$. In **homogeneously aligned** samples of the **former** type they observed **patterns whose** threshold voltage **decreased** monotonically as the temperature was **increased**. They observed an essentially similar type of threshold voltage variation in **homeotropically aligned samples which** had **negative** $\Delta\sigma$ and **positive** $\Delta\epsilon$. They have **concluded** that these **patterns** were due to **electroconvective** processes (see **also, Ribotta and Durand 1979**) **taking place** in the sample, which are essentially independent of the **sign** of $\Delta\epsilon$.

However, our observations on the **electrohydrodynamic** patternn **can** only be explained on the **basis** of **Carr-Helfrich mechanism**. According to **this** theory, the **square** of the threshold voltage is proportional to $\frac{1}{\xi^2 - 1}$.

In the present case, where $\Delta\sigma$ is **negative** and $\Delta\epsilon$ is **positive**, the **Helfrich** parameter **is obtained** by interchanging $\epsilon_{||}$ and $\epsilon_{\perp}$ and **also** $\sigma_{||}$ and $\sigma_{\perp}$ in equation (7.5). **Then**, we get,

$$\xi^2 = \frac{2}{-\Delta\epsilon \epsilon_{||}} f(\eta) \left(\frac{\sigma_{||}}{\epsilon_{\perp}} - \frac{\sigma_{\perp}}{\epsilon_{||}} \right) \quad (7.10)$$

where $f(\eta)$ is a function of the **viscosity** coefficients.

The **Carr-Helfrich mechanism** is operative only if $\xi^2 > 1$. As the **temperature** is raised, the value of $\sigma_{||}/\sigma_{\perp}$ **increases** (Rondelez, 1972) and **consequently** the value of ξ^2 **decreases** approaching the value one. **This explains the increasing trend**

in the value of the threshold voltage with rising temperature in figure 7.7. Once $\frac{2}{\epsilon}$ becomes smaller than one the Carr-Helfrich mechanism becomes inoperative and no instability patterns can be seen. On the other hand, when we approach the nematic-smectic transition point the bend elastic constant and some of the viscosity coefficients increase rapidly resulting in an increase in the threshold voltage [see equations (7.6) and (7.9)]. This explains the variation of threshold voltage with temperature in the vicinity of the nematic-smectic transition point in figure 7.7.

We may also note that (1) the spatial periodicity of the patterns observed at low frequencies is comparable to the sample thickness and (2) dynamic scattering was observed in the samples at voltages above roughly twice the threshold voltage. These observations are compatible with the Carr-Helfrich mechanism of electrohydrodynamic instabilities.

We conclude this chapter by pointing out that Bock et al (1978) have indicated the observation of dynamic scattering in nematics having negative $\Delta\sigma$ and positive $\Delta\epsilon$ in their paper dealing with induced smectic mesomorphism.

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CHAPTER VIII

THE ELECTRO-OPTIC CHARACTERISTICS OF A NEMATIC LIQUID CRYSTAL CELL WITH ASYMMETRICALLY TREATED ELECTRODES

8.1 Introduction

The phenomenon of electrohydrodynamic (EHD) instabilities in nematic liquid crystals having negative $\Delta\epsilon$ has been studied extensively and is well understood theoretically, as pointed out in chapter VII. On the other hand, the observations of EHD instabilities in liquid crystals of strong positive $\Delta\epsilon$ (>2) are relatively few. In chapter VII, we described the EHD patterns seen in nematics having small positive $\Delta\epsilon$ and negative $\Delta\sigma$. In this chapter, we describe an interesting electrooptic effect observed in nematics having large positive $\Delta\epsilon$ and small positive $\Delta\sigma$.

Sussmann (1976) and Barnik et al (1976, 1977) have observed EHD flow patterns in nematics having large positive $\Delta\epsilon$. Depending upon the conductivity of the sample, the applied voltage and its frequency either a fingerprint texture or a ^hsperulite-like pattern was observed in these cases. Barnik et al (1976, 1977) have found only field thresholds for the instabilities observed in nematics having $0 < \Delta\epsilon < 3$. In these cases, they have observed the EHD ROW even in the isotropic phase. On the basis of these observations, they have

Concluded that **the instabilities** are electro-convective in nature and do not depend on the **dielectric** anisotropy. According to them the **anisotropy** of the medium is useful only in the **visualisation** of the phenomenon rather than in causing it. They have made **similar observation** in suitably doped samples of **N-p-methoxybenzylidene-p-butylaniline (MBBA)** having negative $\Delta\epsilon$.

Recently, **Ribotta and Durand (1979)** have studied **EHD instabilities** in **MBBA** at frequencies above the **charge relaxation frequency**. They have observed two distinct types of **instabilities**. An **electro-convective instability** having **cellular flows** with **dimensions comparable** to the sample **thickness** occurs at a relatively low **threshold**. At a higher **threshold**, **dielectric stripes** which result from the **Carr-Helfrich EHD instability** mechanism (**Dubois-Violette et al 1971**) and having much shorter **wavelengths** compared to sample thickness are observed. The **threshold** of the **convective instability** decreases with temperature monotonically and the **instability** could be observed even in the **isotropic phase**. On the other hand, the **threshold** for **dielectric stripes** increases sharply as the **NI transition point** is approached and these stripes do not appear in the **isotropic phase**. These observations show that the **mechanisms** for the two type8 of **instabilities** are quite different.

We have **observed EHD instabilities** in **4'-n-alkyl-4-cyano-biphenyls** which have $\Delta\epsilon > 7$. Further, we have found a **polarity-dependent electrooptic effect** in liquid crystal cells containing

these materials and having asymmetrically treated electrodes.

Sussmann (1978a) has made a detailed study of the rectification action in liquid crystal cells similar to the one used by us. He has suggested a possible mechanism for this rectification action. We will discuss this in a later section and use it to explain the electrooptic effect observed by us.

8.2 Experimental

The experiments were done using the sandwich geometry (see figure 7.1) in which the Liquid crystal is contained between two tin oxide coated glass plates separated by mylar spacers. The oven and sample holder described in chapter VII were used. The thickness of the cell was usually in the range 10-25 μ . The conducting surfaces coming into contact with the liquid crystal were subjected to prior treatment so as to get homogeneous alignment of the sample. Usually one of the electrodes was coated with SiO (silicon monoxide) at an oblique angle of 55-65° with respect to the normal. The thickness of the coating was about 300-500 Å. In many studies the other electrode was rubbed unidirectionally with a filter paper. The resulting cell is similar to the one used by Sussmann (1978a) in his experiments. Instead of rubbing, we also tried to coat the second electrode with different materials. We found that Al_2O_3 (aluminium oxide) is a useful coating material to get good alignment and reproducible results.

The compounds used in our experiments were 4'-n-pentyl-4-cyanobiphenyl (5CB), 4'-n-heptyl-4-cyanobiphenyl (7CB) and E7, a mixture of cyanobiphenyls and cyanoterphenyls marketed by BDH. The observations were similar in all the cases.

The optical observations were made through a polarising microscope using sodium lamp as the source of light. The patterns observed were photographed using a flash light. The experiments were performed using both DC and AC electric fields. The electrooptic response was recorded using a MRD 810 phototransistor of Motorola Company. In the DC studies the signal was amplified using a Keithley microvoltmeter (Model 155) and the current through the sample was measured using an electrometer (Keithley Model 610C). Both the current and the electrooptic response were recorded on a 3-pen recorder (Rikadenki Model B-381H). In the AC studies a Helium-Neon laser was used as the source of light. The output of the phototransistor was amplified using a Burr-Brown amplifier (Model 3640) and was displayed on the screen of a storage oscilloscope (ECIL Model OS768S).

The sample area was about 1 sq.cm. and the typical sample resistance was about a few megohms.

8.3 Observations

DC studies. We will first consider the observations made with a cell having one of the electrodes coated with SiO and the

other one rubbed. The liquid crystal samples already contained some unknown conducting impurities. The resistivities of the samples were in the range of $10^9 - 10^{10}$ ohm cm. Starting with the homogeneously aligned sample, as the DC voltage was increased, the initial director pattern was distorted (Freedericksz transition) at about 1-2 volts. The EHD instability patterns started to appear at about 5 volts. (This voltage was found to vary with the thickness and conductivity of the sample.) Since the threshold is a field threshold, for thin samples (thickness $\sim 6 \mu$) the instability patterns could be seen even at 2 volts. The pattern was usually in the form of small bubbles, but sometimes the fingerprint texture was also seen. The bubbles which looked like maltese crosses between crossed polars were caused by a circular fluid motion in a plane perpendicular to the direction of observation. The EHD motion was distinctly more vigorous when the SiO coated electrode was positive than when it was negative. As was observed by Sussmann (1978a) there was an asymmetry in the DC current also. The current was somewhat higher when the SiO coated surface was positive than when it was negative. However, we must mention that the asymmetry in the current (or rectification) was not as high as that reported by Sussmann in his system which used a Schiff-base formulation and indium oxide coated electrodes. Also we have not tried to normalise the current measurements with reference to the in-phase value, as was done by him. The difference in the electrooptic

response was very evident when the cell was placed between crossed polars. Under the action of an electric field larger than the Freederickss threshold, ^{most of} the molecules of the sample will align perpendicular to the glass plates if there is no EHD instability. Then the system comprising of the cell plated between crossed polarizers will not transmit any light. The presence of ionic impurities gives rise to EHD motion in the sample. This motion disturbs the alignment of the molecules resulting in the transmission of considerable amount of light through the system. In the present case, where the sample has high positive $\Delta\epsilon$ and small positive n_0 , the EHD motion arises due to injection of charges at the boundaries (Felici 1969) or due to electro-convective processes (Barnik et al 1976). When the SiO coated electrode is at a positive potential, the EHD motion is more vigorous and consequently the field of view appears bright (figure 8.1a). On the other hand, when SiO coated electrode is at negative potential the EHD motion is less and the field of view remains more or less crossed out (figure 8.1b).

This was confirmed by observing the scattering of a laser beam by the sample. Under proper conditions, with SiO coated electrode positive there was a strong scattering of light due to the vigorous EHD motion in the medium. Further, the spherulite like flow pattern give rise to a scattering in the form of a ring (figure 8.2). The ring diameter corresponds to the spherulite size being almost equal to the thickness of the sample. When the voltage was reversed the scattering of light was negligible as there was no noticeable EHD motion in the medium.

FIGURE 8.1

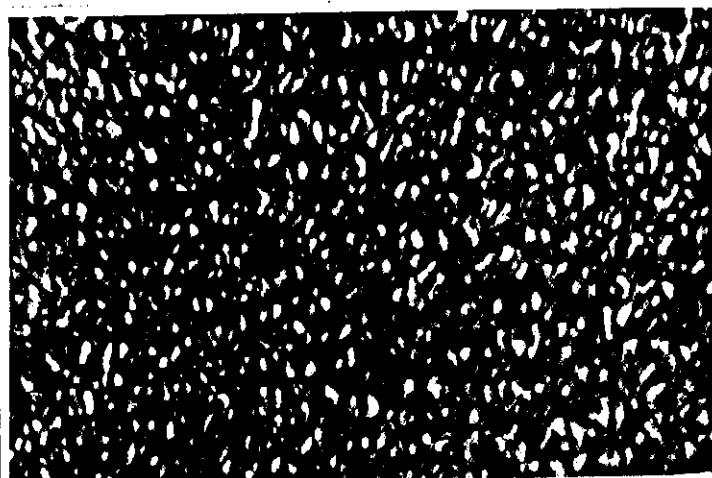
Photomicrographs of the electrohydrodynamic patterns seen in a cell containing K_7 under DC excitation. Crossed polars (x 200) Voltage applied = 30 V.

- a) SiO coated electrode positive
- b) SiO coated electrode negative.

FIGURE 8.2

The diffraction pattern observed when a laser beam is scattered by the cell with the SiO electrode at a positive potential.

a



b

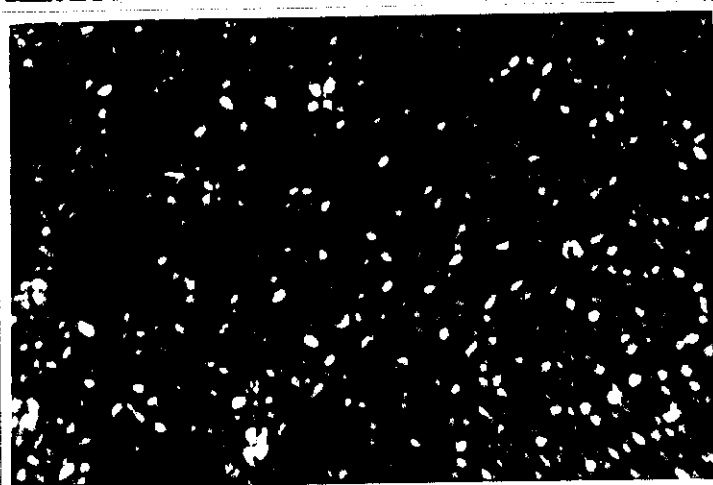


FIG 8-1

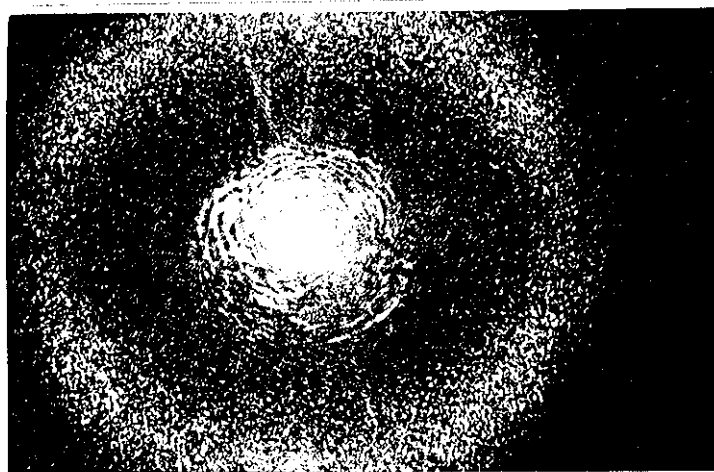


FIG 8-2.

The contrast in the electrooptic response and the current asymmetry were studied as a function of the applied DC voltage. The method was to reverse the polarity using a DPDT switch. The current usually had a transient response which decayed in a few seconds to a steady value. The electro-optic response had a more complicated behaviour. In some samples, immediately after the field was reversed (to make the SiO coated electrode positive) the optical transmission coefficient increased to a high value. Over tens of seconds it reduced to a steady value (figure 8.3). In some other cases, the increase was not so high, but in course of time the intensity gradually attained a steady value as shown in figure 8.4. The optical contrast between the positive and negative voltages increased initially as the voltage increased and an optimum contrast was obtained at about 15–20 volt (for sample thickness in the range 15–20 μ). For very thin ($\sim 10 \mu$) samples the maximum contrast was obtained at comparatively low voltages (~ 4 V).

A further increase in voltage usually reduced the transmitted intensity for both the signs of the applied voltage and lowered the contrast. The current increased with the voltage for both signs of the applied voltage. However, the current asymmetry usually decreased with increase in applied voltage. If the sample is kept under high voltage (~ 40 V) for a long time, the SiO coated surface gets damaged and consequently the alignment of the sample deteriorates.

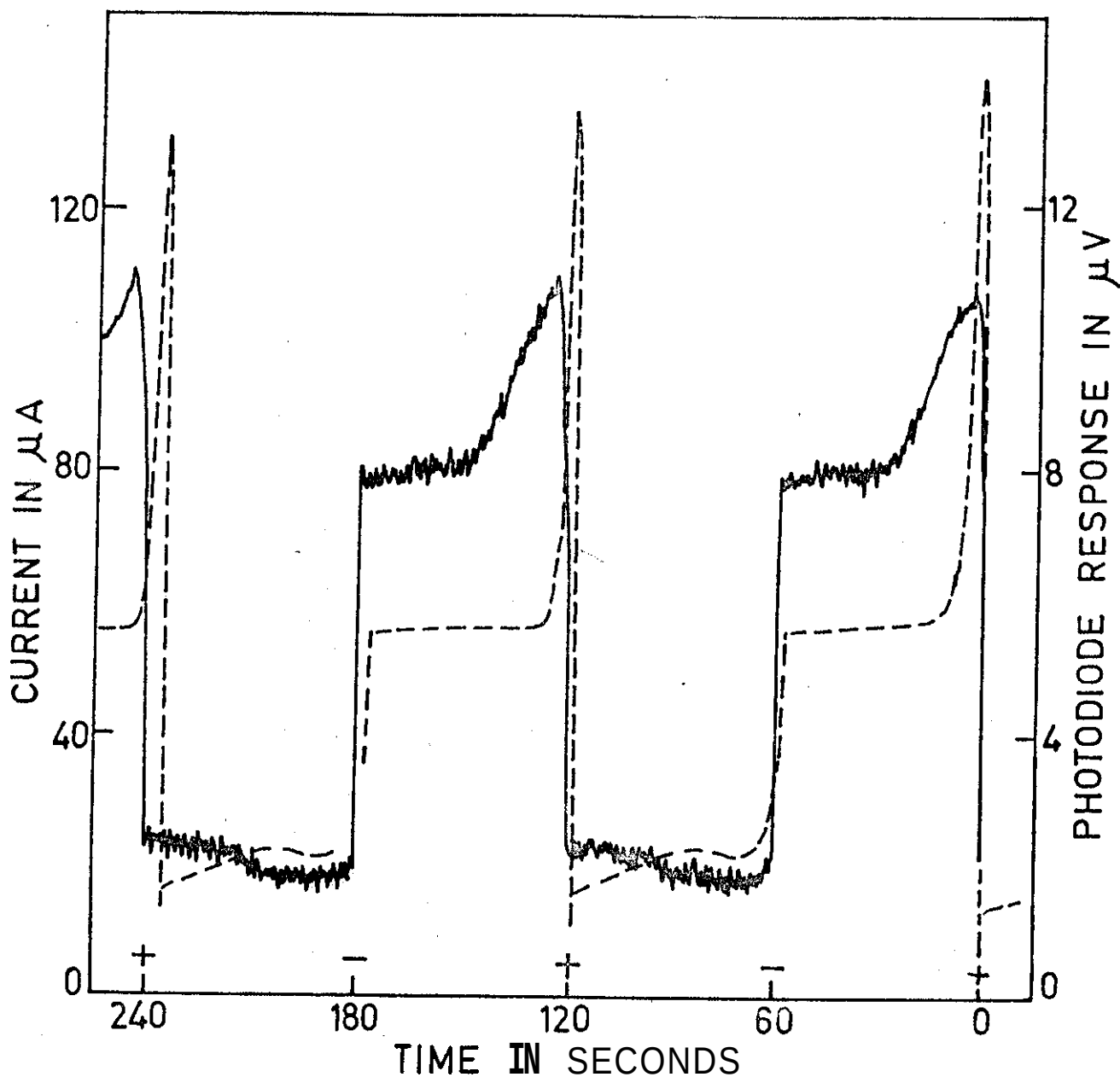


FIGURE 8.3

Electrooptic response (continuous line) in a cell having one electrode coated with SiO and the other one rubbed. The dashed line represents the current. The positive and negative signs at the bottom of the figure stand for the DC polarity to which the SiO coated electrode has been switched. Thickness of the cell $\sim 15 \mu$. Voltage applied is 40 v.

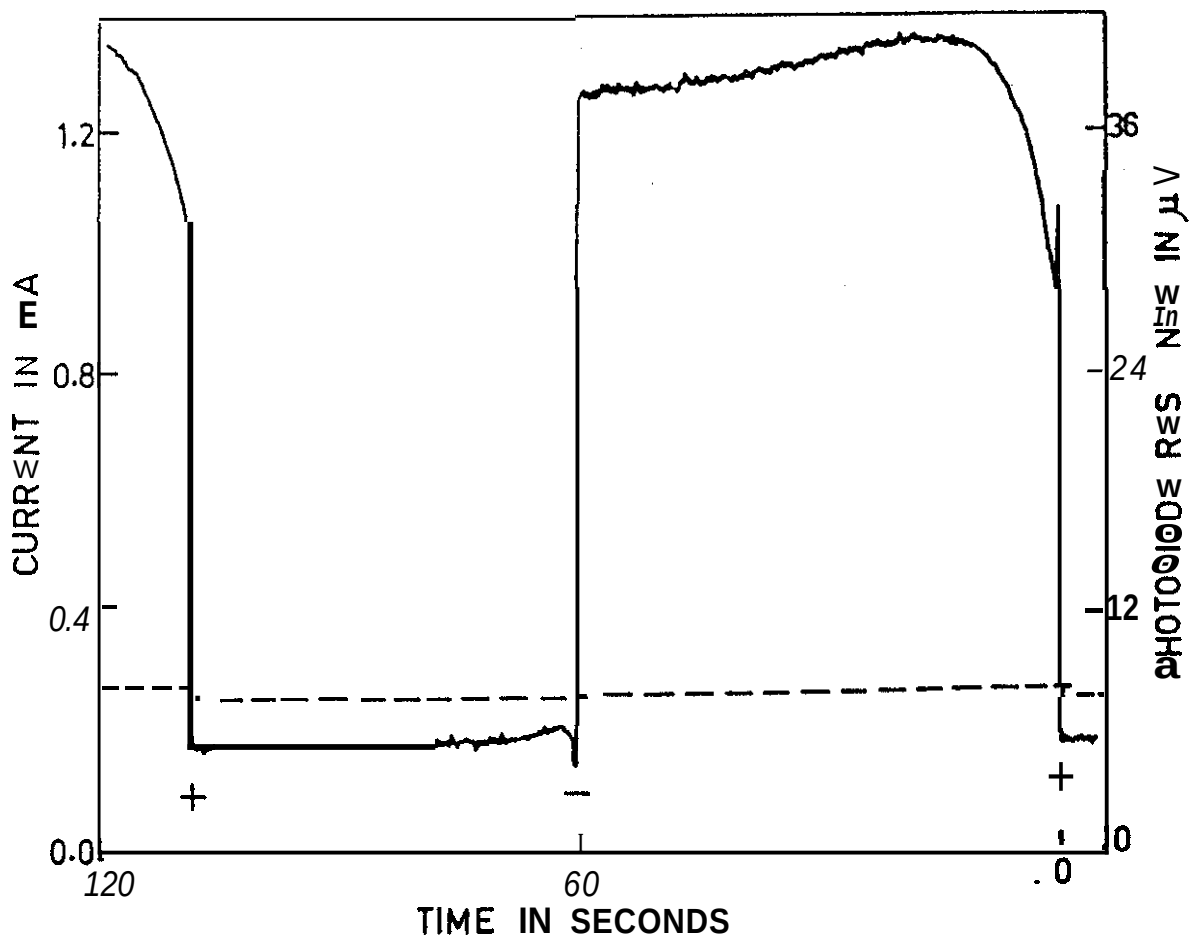


FIGURE 8.4

The electrooptic response in another cell with SiO-coated and Al₂O₃ coated electrodes and containing E₇. Applied voltage is 15 V (other details as in figure 8.3).

AC studies. Host of the studies under AC electric field were done at 20 Hz since Me response was good at that frequency. As the frequency was increased, the threshold field for EHD instability increased ^{see also} (Barnik et al 1976) and the maximum contrast that could be obtained decreased. However we could observe a small asymmetry in the electrooptic response even at a frequency of 1.5 KHz.

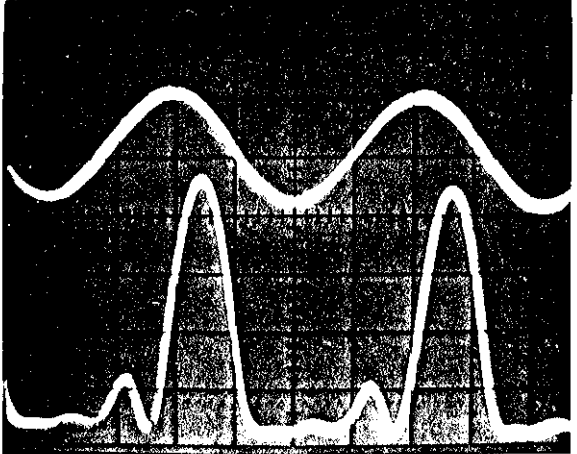
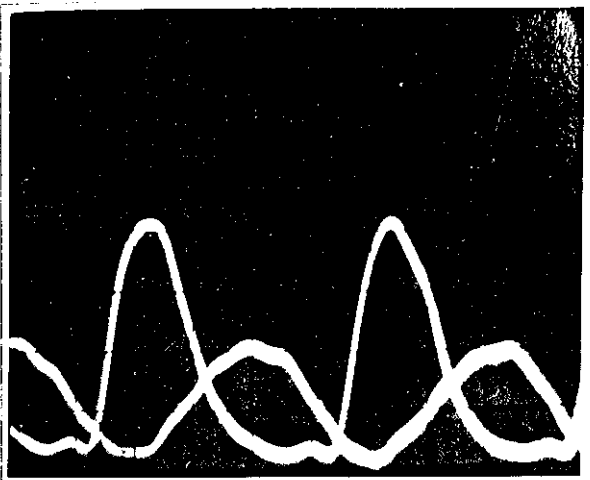
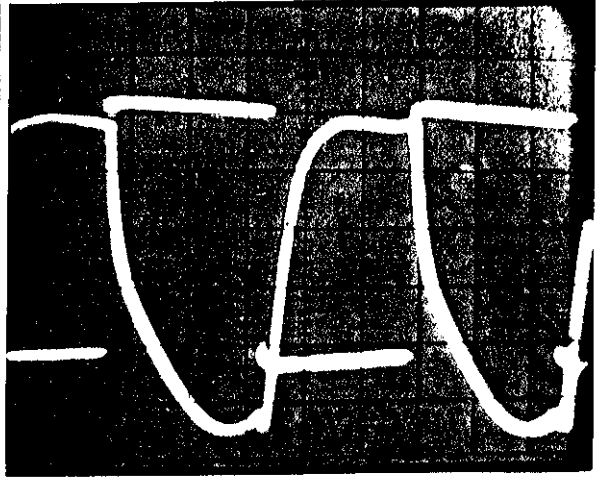
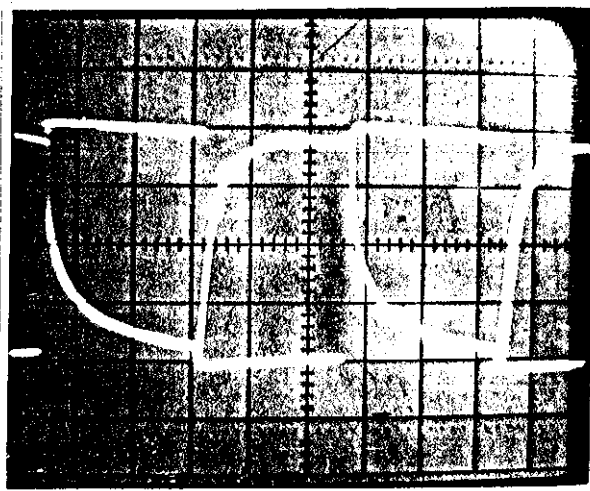
Usually, the best response was obtained when the cell was viewed between crossed polarisers, set at 45° to the undistorted director. Figures 8.5a and 8.5b illustrate the response observed with 20 Hz. Square wave excitation normally gave a somewhat poorer response (Figures 8.5c and 8.5d). Usually, the electrooptic response varied with time, both in AC and DC cases. However, the AC response stabilised after some time and then did not vary even after operating the cell for several hours. The response of the cell was found to be repeatable even after a lapse of one or two days after construction.

The maximum contrast ratios that could be obtained were 1:8 in the case of DC excitation and 1:4 in the case of AC excitation, where we have defined the contrast ratio as the ratio of the peak responses in the two halves of the AC voltage cycle. Probably a more appropriate measure of the contrast would be the ratio of the integrated intensities in the two halves (i.e., the ratio of the areas under the response curves). The maximum contrast is almost the same as given above, even

FIGURE 8.5

The electro-optic response of a cell (with one electrode coated with SiO and the other one rubbed) under AC excitation. The exciting voltage pattern is also shown.

- a) Square wave excitation at 2 V
- b) Square wave excitation at 4 V
- c) Sine wave excitation at 6 V
- d) Sine wave excitation at 10 V.



c

d

when the calculations are done this way.

The electrooptic effect was also studied using electrodes treated in other ways, for example, using a cell having one electrode coated obliquely with SiO and the other one coated obliquely with some other material. It was found that Al_2O_3 is a useful coating material. When glass plates coated with Al_2O_3 at an oblique angle of 55° - 65° are used in the cell, good alignment of the sample was obtained. The electrooptic asymmetry of a cell with one electrode coated with Al_2O_3 and the other one rubbed was very small. But a cell having one electrode coated with SiO and the other one coated with Al_2O_3 gave a fairly good electrooptic asymmetry. The reproducibility of the electrooptic response of such a system was better compared to the SiO coated and rubbed system. However, the transmitted intensity in the former system was somewhat less compared to that in the latter.

Even when the two electrodes were coated with the same material, a small electrooptic asymmetry was observed when the thickness of the coatings were different for the electrodes.

8.4 Discussion

Based on detailed observations on the rectification action of cells with one electrode coated with SiO and the other one rubbed, Sussmann (1978a) has concluded that the negative ions are electroadsorbed more effectively at the positive electrode than

the positive ions at the negative electrode. (Presumably, this arises due to the different rates of electrode reactions for the positive and negative ions.) Hence the current in the liquid crystal sample is carried mainly by positive ions. When the SiO coated electrode is positive the full area of the uncoated electrode is available for the flow of current. On the other hand, when the SiO coated electrode is negative, the positive ions 'see' effectively a reduced area of the electrode and correspondingly the measured current is less. This gives an explanation for the rectification action in such cells. It also explains our observation of asymmetry in the electrooptic response. When the SiO coated side is positive, the current through the sample is higher as compared to the reverse case. Correspondingly there is a more vigorous EHD motion when the SiO coated electrode is positive. Due to the EHD motion, the alignment of the sample gets disturbed and consequently a considerable amount of light passes through the system comprising of the cell placed between crossed polarisers.

As mentioned earlier the nature of the conducting impurities present in the sample is not known. If, as is likely, the impurity is of a salt type, the liquid crystal molecules are also expected to take part in the conduction mechanism (Barrett et al 1976a, 1976b; Lim et al 1977). In order to test the validity of the explanation given above, we carried out an experiment with a sample in which the negative ions were the

majority current carriers. Such a sample was obtained by dissolving 1-2 per cent of an electron-acceptor, via., 7,7',8,8'-tetracyanoquinodimethane (TCNQ) in the liquid crystal. It is now well established that with such redox dopants which have (in the case of acceptors) a reduction potential which is much lower than that of the liquid crystal, the current flow will mainly take place through the redox dopants. Molecules of the redox dopants pick up negative charges at the cathode and the negative ions thus formed get injected into the sample. Hence, we might expect that with the doping, the electrooptic response would be reversed. And it is indeed what was observed. With SiO coated side negative, stronger EHD flow was observed and the contrast was found to be reversed in such samples. Further, when the sample was doped with a salt like cetyl pyridinium bromide, the usual type of contrast was observed i.e., the field of view was brighter when the SiO coated electrode was positive. These observations support the mechanism described above.

In materials having a large positive $\Delta\epsilon$ and a small positive $\Delta\sigma$, the EHD instabilities most probably arise due to electro-convective processes (Barnik et al 1976). The instability patterns become visible in the nematic phase because of the optical anisotropy. The dielectric anisotropy of the material does not play a major role in this mechanism.

Indeed, the asymmetry of electrooptic response of the

liquid **crystals in** sandwich **cells** similar to the one described above can be seen **even in materials** with negative $\Delta\epsilon$ (though the **asymmetry is very small, in these samples**). However, it should be **noted that** at low **frequencies** the instabilities seen in **materials** with **negative $\Delta\epsilon$** arise due to both the **conduction regime of Carr-Helfrich mechanism and electro-convective processes**.

We may finally mention **that** after our **investigation** was completed **Sussmann (1978b)** has made **electrooptic observation** **similar to that made by us and confirmed the asymmetry in electrooptic response of the cells having asymmetrically treated electrodes**.

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