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# Electric-Field-Induced Texture Transformation and Pitch Contraction in a Cholesteric Liquid Crystal†

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**Abstract**—D.C. electric-field-induced pitch contraction and a simultaneous transition from the cholesteric plane texture to the focal conic texture were studied microscopically in a mixture of 20% cholesteryl chloride and 80% cholesteryl oleyl carbonate. The texture change is preceded by the formation of a periodic pattern in the plane texture.

The decrease in helix pitch was determined from selective reflection measurements. The change in pitch $p$ is very small for applied fields less than 25 kV/cm; above this threshold field the decrease is greater: $\mathrm{d}p/\mathrm{d}V = 0.33\,\mathrm{nm/V}$. In the latter region the increase in reciprocal pitch length is proportional to the applied field, in agreement with Meyer's theory. However, the experimental slope is much less than predicted.

## Introduction

During the last few years the electric and magnetic field effects on the structure of the cholesteric plane texture have received much attention and a number of interesting phenomena have been reported. For example, a field induced cholesteric–nematic transition(1–4) and a change in helix pitch as a result of an applied field. In the latter case both an increase(5–7) and a decrease(8) have been noted experimentally.

This paper reports the results of an experimental investigation concerning the d.c. field effect on a mixture of 20% (by weight) cholesteryl chloride and 80% cholesteryl oleyl carbonate,‡ having a

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‡ This mixture was kindly supplied to us by van Schuppen Chemie, Veenendaal-Holland.

cholesteric–isotropic transition temperature of 38 °C. The mean refractive index of the sample $n_D$ was 1.511 at 28 °C, while the mean dielectric constant was 2.50 at 25 °C. The mixture which is stable at room temperature exhibits selective scattering in the visible part of the spectrum. The wavelength of the scattered light had a low temperature coefficient, viz., $\Delta\lambda/\lambda = 4.10^{-3}$ per °C.

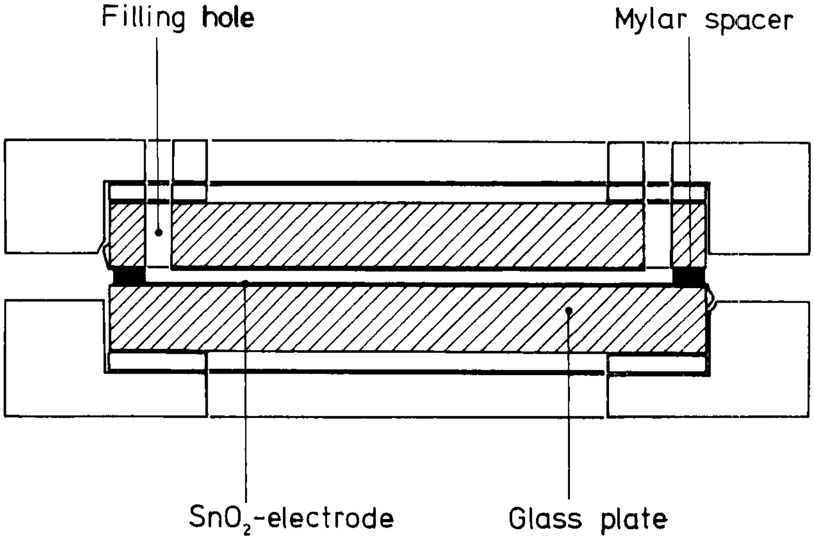

Figure 1. Sample cell.

## Experimental

For the measurements the conventional experimental sample cell shown in Fig. 1, was used. The liquid crystal was held between two glass plates, each covered with a transparent, conducting, tin oxide electrode. The plates were spaced by a mylar sheet about 12 $\mu$m in thickness. The sample was contained within a 1 cm diameter hole in the sheet. Care was taken to ensure that the hole, prepared by a photo etching technique, had very flat edges.

After clamping the plates, the cell was filled with the isotropic melt by capillary action using one of the filling holes in the upper glass plate. The cell was then cooled to room temperature and the electrode spacing $d$ was checked by a capacity measurement which

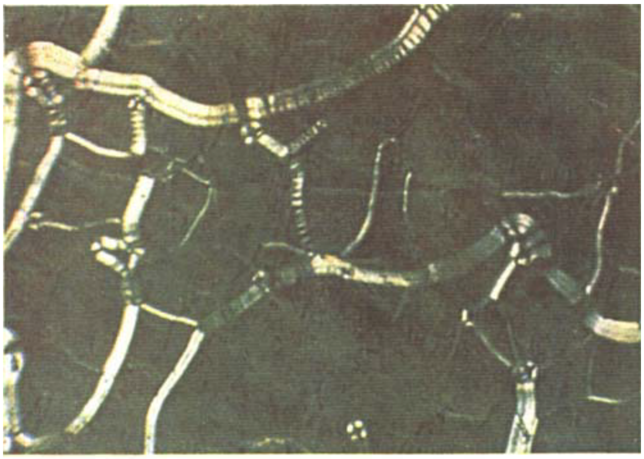

Figure 2. "Disinclinations" in the plane texture. Crossed polarisers, monochromatic light, magnification 200 ×.

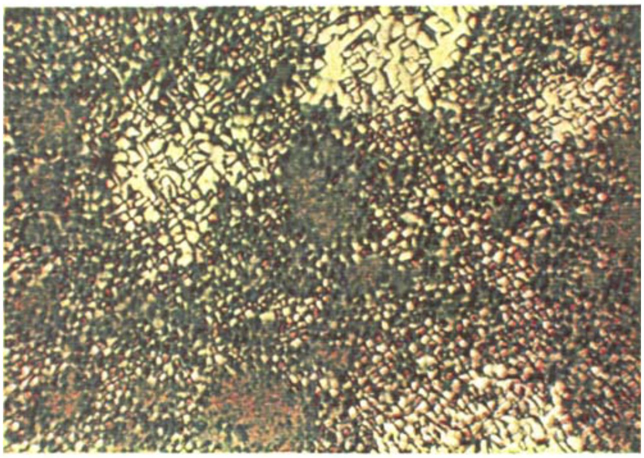

Figure 3. Field-induced cellular birefringent domains and focal conic regions: part of the film has relaxed back to the plane texture. Crossed polarisers, white light, magnification 200 ×.

Figure 4. Field-induced focal conic texture. Crossed polarisers, white light, magnification 200 ×.

yielded a value of 11.5 $\mu$m, in good agreement with the thickness given for the mylar sheet.

At room temperature the sample film is almost everywhere in the undisturbed state.(9) In this texture there are, however, fibre-like regions where the film adopts the plane texture with spherical and cylindrical " disinclinations ". A microscopic view of this non-uniform plane texture is given in Fig. 2. These structures resemble the ones found by Chistyakov(10) in other mixtures of cholesteric liquid crystals.

The whole film acquired the plane texture after a slight displacement of the glass plates with respect to each other. The film was observed to have a bright green colour, thus assuring that the helices of the twisted structure were perpendicular to the electrodes.

If a d.c. voltage is applied to the cell a colour-shift from green to green–blue was observed which indicates that the helix pitch has been decreased by application of a field parallel to the helix axis. At low voltages this effect was not accompanied by a perceptible change in the texture of the film. When the voltage was switched off, the sample returned to its original state in a time of the order of 50 ms. This speed of response is of the same order of magnitude as found by Harper.(8)

At higher applied voltages the colour change was accompanied by the formation of a more or less periodic " cellular " structure in the plane texture. This structure became clearer as the applied voltage was increased. The diameter of the cells was about 3 $\mu$m. At potentials above 30 V the cells became very clear between crossed polarisers as white domains with dark edges. The periodicity of the structure was not voltage dependent. These regular patterns possibly resemble the cellular domains found in some nematic liquid crystals.(11) However, in contrast to the nematic domains no periodic material flow was observed in the cells. At about 30 V the birefringent domains coalesced slowly to a more stable texture which resembles the focal conic texture. At this voltage the colour shift to the blue became more pronounced, while the intensity of the selectively reflected light decreased somewhat due to the formation of the focal conic regions. After switching off this voltage the birefringent domains were transformed again to the plane texture within about 15 minutes; the focal conic regions were noted to be stable for a much longer time. These effects are shown in Fig. 3, where in one picture the focal conic regions, the birefringent domains and the plane texture regions are present.

At still higher voltages, e.g. 60 V, the transition from the plane texture to the focal conic one via the birefringent domains were noted to be practically complete within several minutes. A substantial weakening of the film colour was noted with a concomitant increase in turbidity. After removal of the field, the induced focal conic texture was stable for days. A microscopic picture of this texture is shown in Fig. 4.

In addition to the microscopic observations, optical measurements were performed using selective reflection to estimate the pitch length of the helix as a function of applied field. For these measurements, which were carried out at a temperature of 28 °C, use was made of a Hilger and Watts' Monospek 1000 monochromator. The sample was mounted on a revolving spectrometer stage. A schematic diagram of the equipment is given in Fig. 5. The reflection-band of the film was measured as a function of sample voltage at different observation angles $R$ with a fixed angle of incidence $I=30°$.

The value of $R$ was adjusted from 15° to 45° in 5° steps. No measurements were done at the reflection angle $R=30°$, since specular reflections of the glass surfaces were interfering. At zero field, the peak intensities decreased rapidly at increasing $|R-30°|$-values. The intensity ratio for the $R=25°$ and the $R=15°$ peak was, for instance about 5. This meant that although the Bragg scattering sites were distributed about an orientation where the helix axes are perpendicular to the surface, the deviations from this preferred direction were small. It is easily calculated, for instance, that reflections at $I=30°$ and $R=15°$ correspond to scattering sites with a deviation of $+4°44'$ from the perpendicular orientation; for the $I=30°$, $R=45°$ the corresponding deviation is $-4°17'$.

The results of the electrical measurements are shown in Fig. 6 where the centre of the reflection band, $\lambda_{\text{peak}}$, is plotted as a function of sample voltage. For all observation angles the change in colour is small for an applied voltage of less than 30 V.

At higher voltages the decrease is more rapid and amounts to a shift of about 10 nm per 10 V. Above voltages of 55 V, the measurement of the selective reflection became difficult since the intensity

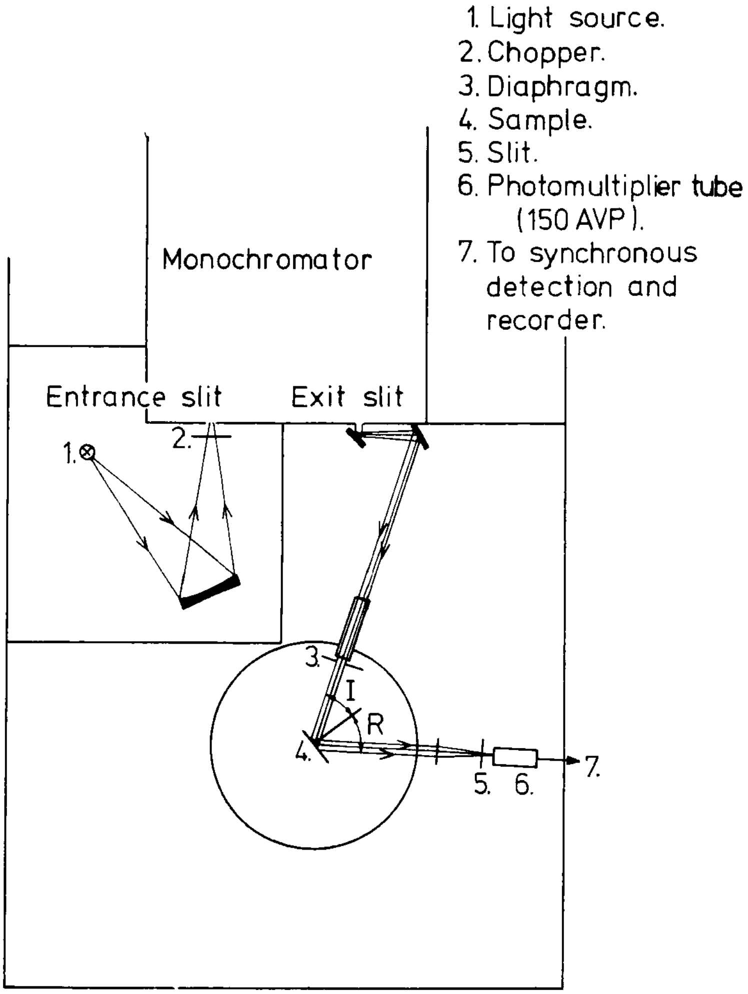

Figure 5. Schematic diagram of the apparatus.

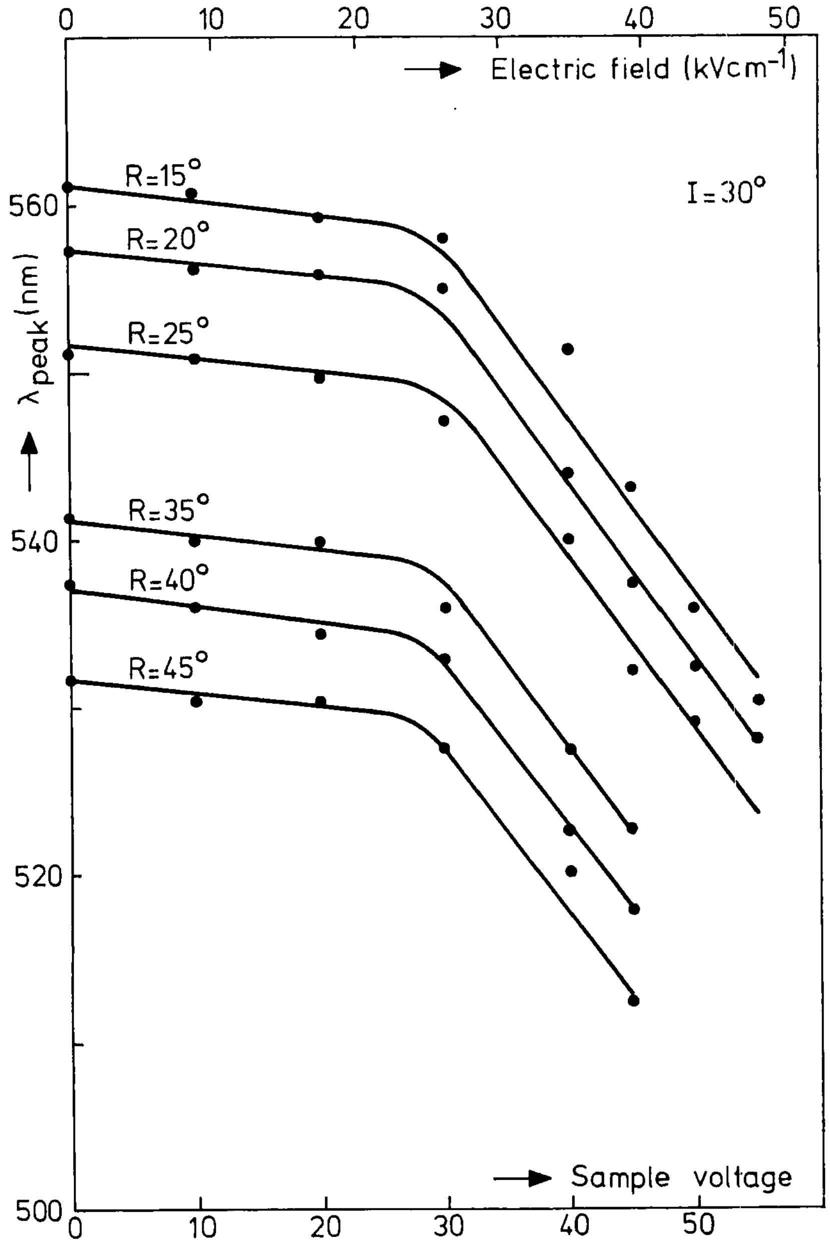

Figure 6. Peak wavelength of the selective reflection band as a function of sample voltage at different angles of observation.

of the diffusively scattered light—caused by the focal conic regions—predominated.

From the data presented in Fig. 7 the pitch $p$ was calculated using the well-known relation:

$$\lambda_{\text{peak}} = 2np\cos\frac{1}{2}\left[\sin^{-1}\left(\frac{\sin I}{n}\right) + \sin^{-1}\left(\frac{\sin R}{n}\right)\right] \tag{1}$$

where $n$ is the refractive index. Figure 7 shows the averaged pitch values as a function of sample voltage. Above a threshold voltage the pitch decreased linearly with the field: $\mathrm{d}p/\mathrm{d}V = -0.33$ nm/V.

The threshold voltage obtained by extrapolation was 28 V.

## Discussion

The theoretical relationship between the pitch length and an applied field parallel to the helix axis has been calculated by Meyer(2) for the case where the static dielectric constant of the cholesteric film in a direction perpendicular to the helix axis is larger than its component parallel to this axis. Since the dipole moment for cholesteryl chloride is approximately parallel to the long molecular axis,(12) this requirement is satisfied for these molecules if they have a preferential orientation in a direction perpendicular to the helix axis. Assuming that the aligning forces of the walls will maintain the helix perpendicular to the wall, so that the only effect of the field is a rotation of the individual molecules in the field direction, Meyer derived a linear dependence between the helix wave vector $q \equiv \pi/p$ and the applied electric field $E$. This relation is valid for fields above a threshold field $E_{\text{thr.}}$:

$$E_{\text{thr.}} = \left(\frac{4\pi k_{33}}{\Delta\epsilon}\right)^{1/2} \cdot q_0 \tag{2}$$

In Eq. (2), $\Delta\epsilon$ is the anisotropy in the dielectric constant, $k_{33}$ is the elastic modulus for bending and $q_0$ is the value of the helix wave vector corresponding to the zero field pitch value $p_0$. Equation (2) is only valid provided $k_{22} > k_{33}$ and $d \gg p_0$; $k_{22}$ is the elastic modulus for torsion and $d$ is the thickness of the sample. Below $E_{\text{thr.}}$, the pitch will be independent of the field.

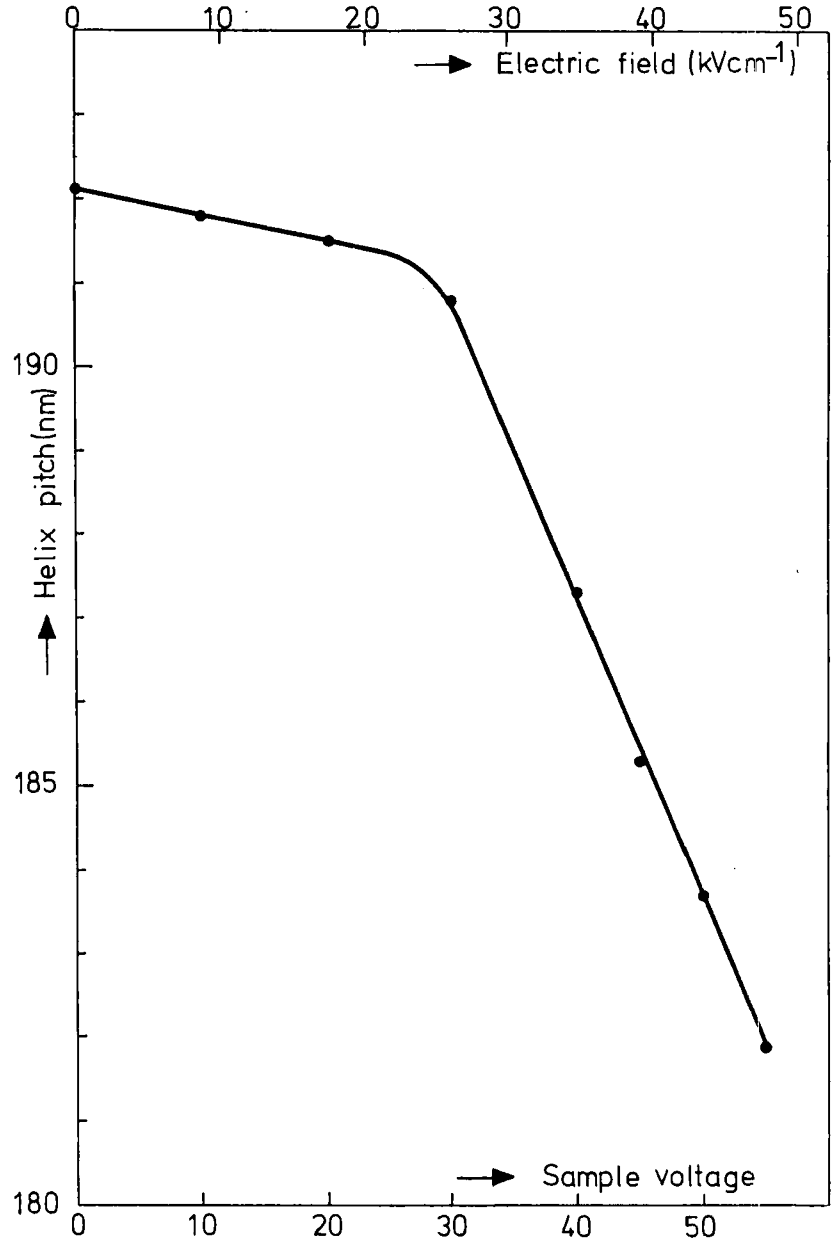

Figure 7. Helix pitch as a function of sample voltage.

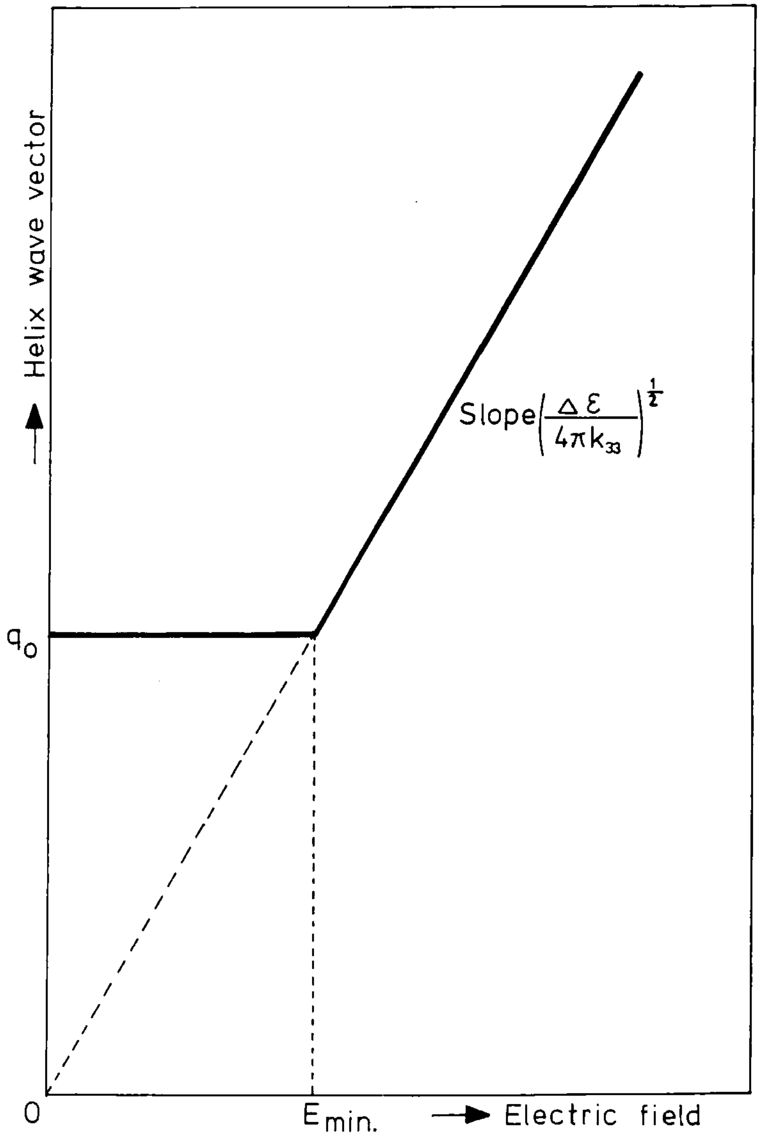

Figure 8. Theoretical $q$–$E$ curve (schematically).

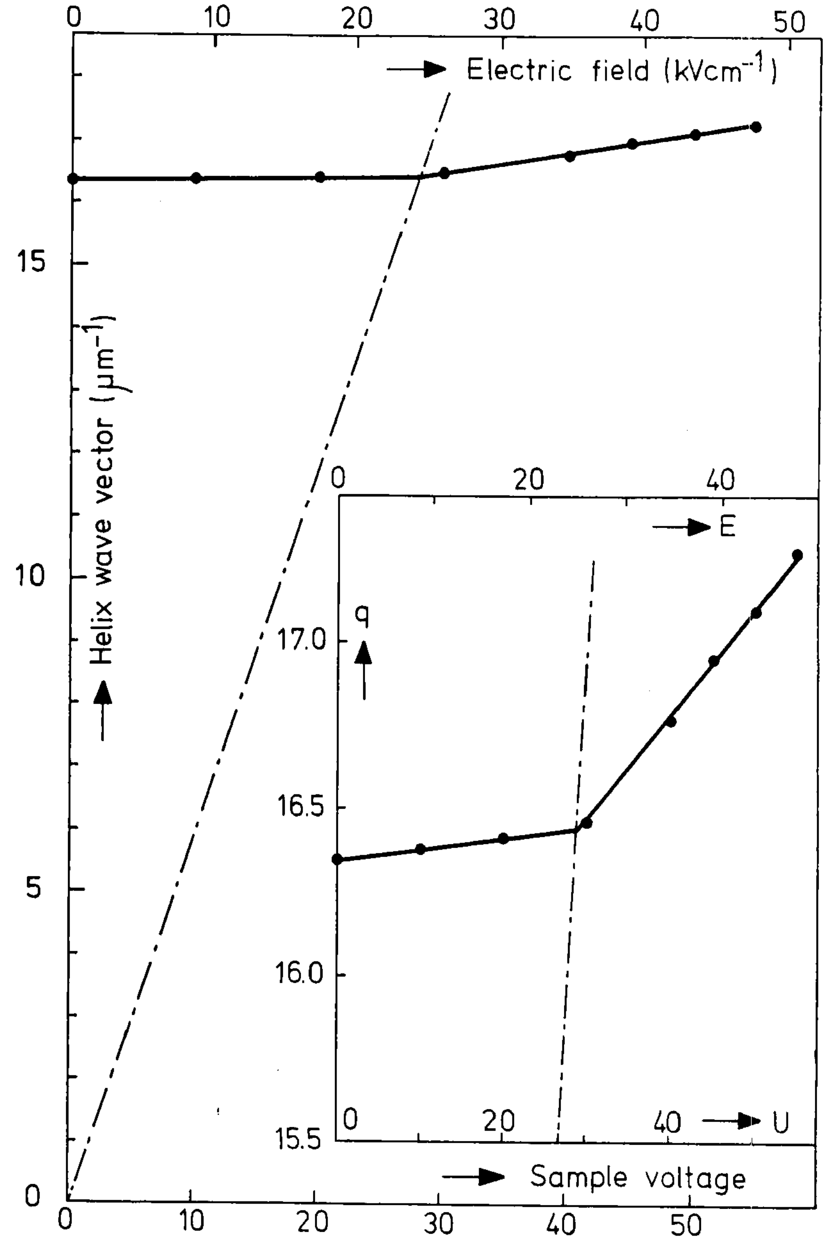

Figure 9. Helix wave vector versus applied field. ——— experimental curve. ·—·—·— theoretical curve drawn through $E_{\mathrm{thr.}}$ and the origin.

The relation between the helix wave vector and the applied field for $E > E_{\text{thr.}}$ is given in Eq. (3):

$$q \equiv \frac{\pi}{p} = \left(\frac{\Delta\epsilon}{4\pi k_{33}}\right)^{1/2} E \tag{3}$$

The theoretical dependence between $q$ and $E$ is given in Fig. 8.

The experimental values of $q$, obtained from the corresponding $p$-values are shown in Fig. 9. Above the threshold field of 25 kV/cm there is a linear relationship between $q$ and $E$ as predicted by Meyer. With the exception of this, however, the results are not in agreement with the theoretical predictions since the extrapolated $q$ versus $E$ line does not intersect the $q$-axis at the origin but at a point slightly below $q_0$. Thus the slope of the experimental curve is much lower than that of the theoretical curve drawn through $E_{\text{thr.}}$ and the origin. This difference in slope is about a factor of 18.

The value of $k_{33}/\Delta\epsilon$ was obtained by inserting the experimental values for $E_{\text{thr.}}$ and $q_0$ in Eq. (2). The result was $k_{33}/\Delta\epsilon = 2.1 \times 10^{-8}$ dyne at 28 °C. Unfortunately the value of $\Delta\epsilon$ and $k_{33}$ are not known for the cholesteryl chloride-cholesteryl oleyl carbonate mixture so that it is not possible to verify the results.

The analytic expression for the experimental results above $E_{\text{thr.}}$ is

$$q = cE + q^* \tag{4}$$

In this expression the constants $c$ and $q^*$ are $37 \times 10^{-2}\,\text{V}^{-1}$ and $15.5\,\mu\text{m}^{-1}$ respectively with $q$ in $\mu\text{m}^{-1}$ and $E$ in V/$\mu$m.

In view of the observed discrepancy between experiment and theory it is important to mention that strong selective scattering effects were observed in transmission at the moment that the field-induced birefringent domains appeared clearly. Since these effects were only observed when the helix axes are parallel to the walls(13) it must be concluded that at fields above the threshold value helices are rotated by the field over 90°. This means that at least one of the assumptions of the model proposed by Meyer is not valid in our situation. It seems reasonable to suppose therefore, that in order to obtain better agreement between theory and experiment, the influences of the surface forces on the molecules in the film need to be accounted for more comprehensively in future theories.

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REFERENCES

1. Sackmann, E., Meiboom, S. and Snijder, L. C., *J. Am. Chem. Soc.* **89**, 5981 (1967).
2. Meyer, R. B., *Appl. Phys. Letters* **12**, 281 (1968).
3. Gennes, P. G. de, *Solid State Commun.* **6**, 163 (1968).
4. Wysocki, J., Adams, J. and Haas, W., *Mol. Cryst.* **8**, 471 (1969).
5. Durand, G., Léger, L., Rondelez, F. and Veyssié, M., *Phys. Rev. Letters* **22**, 227 (1969).
6. Meyer, R. B., *Appl. Phys. Letters* **14**, 208 (1969).
7. Kahn, F. J., *Phys. Rev. Letters* **24**, 209 (1970).
8. Harper, W. J., *Mol. Cryst.* **1**, 325 (1966).
9. Adams, J., Haas, W. and Wysocki, J., *Mol. Cryst.* **8**, 9 (1969).
10. Chistyakov, I. G., *Sov. Phys.-Crystallogr.* **7**, 619 (1963).
11. Durand, G., Veyssié, M., Rondelez, F. and Léger, L., *C.R. Acad. Sci.* (*B*) 270, 97 (1970).
12. Baessler, H. and Labes, M. M., *J. Chem. Phys.* **51**, 1846 (1969).
13. Adams, J. E., Haas, W. and Wysocki, J., *J. Chem. Phys.* **50**, 2458 (1969).