Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: J. C. Lee , D. W. Allender & V. D. Neff (1992): The Effect of Homeotropic Surface Anchoring on the Critical Voltage for Unwinding the Cholesteric Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 210:1, 11-20

To link to this article: http://dx.doi.org/10.1080/10587259208030754

Mol. Cryst. Liq. Cryst., 1992, Vol. 210, pp. 11–20
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Printed in the United States of America

The Effect of Homeotropic Surface Anchoring on the Critical Voltage for Unwinding the Cholesteric Phase

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(Received June 19, 1991)

Experimental data are presented for the unwinding of the helical cholesteric structure in the presence of an applied electric field. Homeotropic surface anchoring conditions are known to reduce the magnitude of the critical unwinding voltage which depends on helical pitch and cell thickness. The experiments are unique in that the pitch is varied continuously at constant cell thickness rather than changing thickness at constant pitch. This is accomplished by employing cholesteric mixtures in which the inverse pitch changes linearly with temperature in the nematic compensation region.

A model introduced by Cladis and Klemen, and extended by Goossens, is used to explain the effect of surface anchoring in the absence of an applied field. The calculations are extended to include the effect of the field, and the theory predicts a universal critical voltage curve involving the product of cell thickness and inverse pitch which is verified by experiment.

INTRODUCTION

In the past several years considerable effort has been focused on understanding the effects of boundary surfaces and applied fields on the untwisting of large pitch cholesteric materials.[1–14] In particular, electric or magnetic fields applied perpendicular to the sample surface, in a mixture with positive dielectric anisotropy, can induce different textures which ultimately will undergo a transition to the untwisted homeotropic phase. The characterization of these field and surface induced textures, including hysteresis effects, has been considered by a number of investigators.[2,3,7,8,11,12,14] In sufficiently thin samples with strong homeotropic anchoring conditions, one invariably observes the so-called fingerprint texture.[2,3] This structure is characterized microscopically by a series of alternating light and dark stripes of well defined periodicity. The direction of the helical twist axis is known to be essentially parallel to the plane of the surface and perpendicular to the stripes.[9] Applied electric or magnetic fields lead to an untwisting of the structure by a mechanism first described by de Gennes for the infinitely thick film. He has classified this cholesteric to homeotropic (CH) transition as being of the nucleation type.[1] Hysteresis effects are observed in the reverse homeotropic-cholesteric transition (HC) and have been of interest because of possible application in display

devices.[13] It is found that the effect of surface anchoring is very important in thin films and, as a result, film thickness is a significant factor. Most of the reported work has been concerned with the effect of the (d/p_0) ratio on the magnitude of the critical field. Here d is the film thickness and p_0 is understood to be the pitch which would be observed in bulk samples in the absence of applied fields and strong surface anchoring.

In most of the previously reported work, the sample thickness was varied at constant pitch. This requires either creating a thickness gradient in a wedge type cell or the preparation of separate samples using different spacers.[9,13] In this paper, following the work of Shashidharan,[11] we report on similar experiments, but we vary pitch continuously in a cell of constant thickness. This is accomplished by taking advantage of the remarkable phenomenon of the temperature compensation of pitch in certain mixtures of cholesteric or cholesteric and nematic compounds.[11,15] In these mixtures the inverse pitch varies linearly with temperature in a region close to the nematic compensation temperature where it goes to zero (i.e. infinite pitch). We believe that these measurements have the advantage that pitch (or twisting power) can be varied continuously without disturbing the surface anchoring conditions and without creating thickness gradients in the cell. In the results reported here we consider only the homeotropic (or perpendicular) anchoring conditions. Even under these restricted conditions we must distinguish between strong and weak surface anchoring. The lack of this distinction has led to some confusion in the existing literature.[12] In thin samples strong anchoring conditions invariably give the fingerprint texture which is characterized by a pitch p which is larger than the natural pitch p_0. On the other hand weak homeotropic anchoring, in the absence of external fields, gives the so-called focal conic texture, which is characterized by a microscopic periodicity which is close to the natural (undistorted) pitch.[8] In this case, the direction of the helical axis is presumed to be tilted with respect to the surface plane. The results reported here are concerned with the critical field for the CH transition under strong anchoring conditions but we have also measured the periodicity in the focal conic texture in order to determine $q_0 = 2\pi/p_0$.

EXPERIMENTAL

The liquid crystal used was a compensated mixture of cholesteryl chloride (CC) and 4-cyano-4′-*n*-octylbiphenyl (8CB) in a 1:1 weight ratio. The CC was purified by recrystalization and the purified 8CB was used as received from BDH Ltd. The nematic compensation temperature of this mixture (where the undistorted pitch becomes infinite) is 36.3°C.

Cholesteric pitch measurements were made in cells with both the focal conic and the fingerprint texture. In the former, weak surface anchoring was achieved by treating flat glass plates with chromic acid. For the latter, the plates were cleaned with chromic acid and dipped in a 0.2% Alconox solution.[12] In the focal conic texture the pitch, which is presumed to be essentially that of the undistorted helix, was determined from the microscopic pattern which has a periodicity of about $p_0/2$.[16] For strong homeotropic anchoring the pitch p was determined by measure-

ment of the diffraction rings and also by the microscopic periodicity produced by the fingerprint texture.[8] Both measurements gave the same value of q within experimental error. In order to obtain a sharp diffraction pattern it was necessary to apply a weak electric field less than 50% of the threshold value. It is known that the pitch p is little affected by applied fields, except in the critical region very close to the CH transition.[8]

The effect of applied electric fields was determined by placing the mixture between flat glass plates coated with transparent indium tin oxide. Strong homeotropic orientation was obtained by immersing the plates in a 0.2% Alconox solution. Teflon films were used as spacers and the cell thickness was assumed to be that of the spacer. The glass plates were placed in a modified Perkin Elmer heated infrared cell and the temperature was controlled to 0.02°C with a YSI Model 72 proportional controller. The cell was placed between crossed linear polarizers in the light path of a helium neon laser. Transmitted light was detected with a photodiode. The (CH) phase transition was induced by both DC and 1.1 kHz AC electric fields.

RESULTS AND DISCUSSION

1. Variation of Pitch with Temperature

It is well known that certain binary mixtures of cholesteryl esters will undergo a linear change in inverse pitch ($q_0 = 2\pi/p_0$) with change in composition or temperature.[11] It is perhaps less well understood that similar behavior is observed with certain mixtures of cholesteric and nematic compounds.[15] For studying the effects of surfaces and applied fields, the latter materials have some advantage because of the generally larger values of the dielectric anistropies and surface anchoring forces. For the temperature compensated mixture of CC and 8CB we introduce the relation

$$T - T_c = \Delta T = q_0/\beta \tag{1}$$

where T_c is the nematic compensation temperature for the bulk mixture. The slope $\partial q_0/\partial T = \beta$ is a fundamental parameter relating temperature to the cholesteric twisting power. For the 1:1 mixture of CC with 8CB, $\beta = 0.20$ as determined from the slope of the plot of q_0 vs ΔT as shown in Figure 1. Also shown in the figure is a plot of q vs ΔT as determined from the interference rings of the fingerprint texture. It is found that the slopes of both curves are essentially the same within experimental error and this result will have considerable significance in our later discussion. It is also to be noted that the distorted wave vector q does not go to zero with ΔT. In fact q drops abruptly to zero at a temperature ΔT^* as shown in the figure. This is related to the fact that, in thin films with strong homeotropic anchoring, the CH transition is induced by the surface conditions even in the absence of an applied field. It is also found that ΔT^* [i.e., inverse pitch by Equation (1)] is inversely proportional to the sample thickness d with the relation $(d/p_0)^* = 0.74$ for the given mixture. This independent measurement will be verified by the experiments with electric fields to be discussed in the following section.

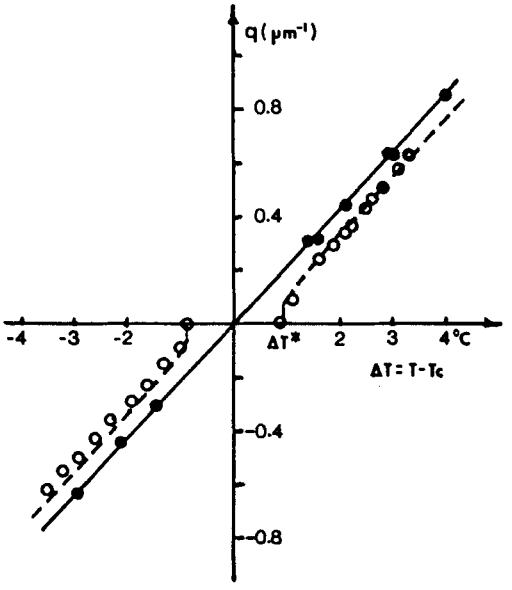

FIGURE 1 A plot of $q_0 = 2\pi/p_0$ (solid circles, weak anchoring) and q (open circles, strong anchoring) vs. ΔT for a 1:1 mixture of CC and 8CB. The sample thickness was 25.4 μm. The slope $\beta = q_0/\Delta T = 0.20\ (\mu m)^{-1}/°C$ is the same (within experimental error) for both sets of data. With strong anchoring the fingerprint texture undergoes a transition to the homeotropic phase at ΔT^*. The dotted line was calculated from Equation (11) using the best fit parameters from the data in Figure 3.

2. Effect of Applied Electric Fields

The optical effects of applied electric fields were studied with polarized light as discussed previously. We obtained similar, but not identical, data with both DC and AC fields. We believe that some sample electrolysis occurred over the long equilibration periods required to obtain the DC data so we report only that for AC fields at 1.1 KHz. The threshold voltage as a function of ΔT is shown in Figure 2 for three different cell thicknesses. There are several remarkable features associated with these voltage vs. inverse pitch phase diagrams. First of all, we note the symmetry of the coexistence lines with respect to the sign of ΔT. This tends to confirm the independent observation that inverse pitch varies linearly with temperature over the range of the measurements ($\pm 4°C$) in regions of positive and negative pitch. Secondly we note the linearity of the coexistence curves over a wide range of values of ΔT. This is consistent with the result of de Gennes for the untwisting of bulk cholesterics.[1] In terms of our experimental parameters, the de Gennes formula is

$$V_c = \pi[(K_{22}/\varepsilon)^{1/2}\ \beta d\Delta T]/2 \tag{2}$$

where d is the cell thickness, K_{22} is the elastic constant for twist, and $\varepsilon = (\Delta\varepsilon)\varepsilon_0$ where $\Delta\varepsilon$ is the dielectric anistropy and ε_0 the vacuum permitivity. Finally, we draw attention to the abrupt decrease in threshold voltage at temperature ΔT^*

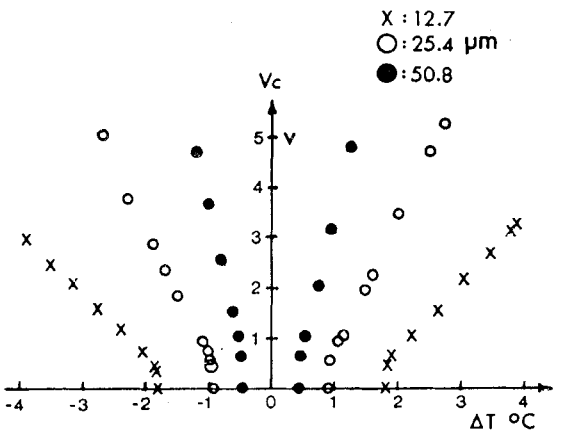

FIGURE 2 Critical voltage vs. ΔT for the cholesteric-homeotropic transition of a 1:1 mixture of CC and 8CB. The sample thickness (in μm) is shown on the plot. The coexistence line terminates at temperature ΔT^* when $V_c = 0$. ΔT^* is found to be inversely proportional to cell thickness.

(i.e. pitch p_0) in the phase diagram. This behavior is not consistant with the results of bulk samples, i.e. with Equation (2).

It is instructive to compare the above results obtained by changing undistorted pitch at constant d with some of the previous results others have obtained by changing d at constant pitch. The comparison is made only for homeotropic anchoring conditions in the region where the cholesteric phase assumes the fingerprint texture. Gerber has observed the linear variation of V_c with d [Equation (2)] in a wedge-type cell with fixed pitch.[9] His results also show that the threshold voltage is reduced by a constant amount below the de Gennes limit. He observed a critical thickness in the absence of an electric field at a value $(p_0/d) = 0.98$. Gerber relates the data to an asymptotic expansion in powers of p_0/d. Sprang and van de Venne also considered the CH transition by measuring the threshold voltage in cells with different spacers.[13] They accounted for the influence of the surface orientation by specifically introducing surface free energies for different anchoring conditions. For the CH transition they obtain the equation

$$V_c = [8\pi^2(d/p_0)^2 K_{22}/\varepsilon - 8Fd/\varepsilon]^{1/2} \tag{3}$$

where F is a free energy per unit surface area. The equation is weakly nonlinear in d/p_0 and gives a reasonable fit to their data which, however, are quite scattered. No abrupt drop in critical voltage is reported. Equation (3) does not give a good fit to our data for any values of the parameters K_{22}/ε or F.

From Figure 2 it is established that the slopes of the coexistence lines are directly proportional to cell thickness. Thus, all of the data can be plotted on a universal curve as a function of $d\Delta T$ (or dq_0) as shown in Figure 3. This fundamental scaling relation is of considerable theoretical interest because it implies that any derived expression for V_c should be a function only of the dimensionless product variable $q_0 d$.

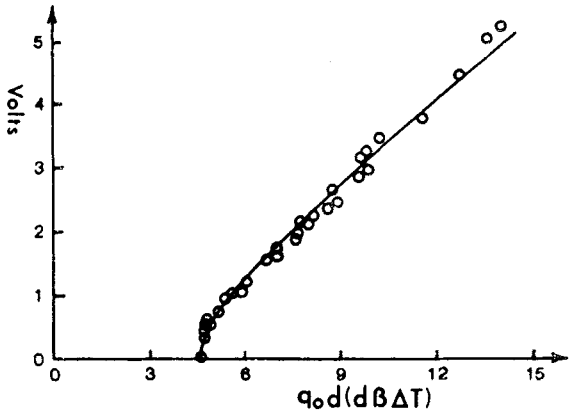

FIGURE 3 Universal plot of critical voltage vs. $q_0 d$ for a 1:1 mixture of CC and 8CB. The open circles were obtained from all three sample thicknesses shown in Figure 2. The solid line represents the best fit of the data to Equation (16).

3. The CH Transition in Zero Field

Most attempts to explain the field dependence of the CH transition have been based on the assumption of strong anchoring so that the contribution of surface orientation to the free energy density is contained entirely in the surface boundary conditions. The major constraint to obtaining an exact theory is that, in the chiral (fingerprint texture) phase, the director n is not constrained to a single plane so the free energy has to be minimized with respect to three independent variables involving all three of the elastic constants. Press and Arrot have carried out detailed computer calculations on the morphology of the fingerprint texture.[4,5] Their results do not lead to an analytical expression for the free energy density and, as stated by Goossens, can probably be replaced by simpler lower dimensional models without causing serious error in the equations describing the effect of applied fields.[10] A tractable simplified model involving homeotropic surface alignment was first introduced by Cladis and Kleman[2] and later extended by Goossens.[10] The fundamental assumption is that the helical axis lies parallel to surface boundaries (the z axis) and according to the optical properties of the fingerprint texture there is translational invariance along the y axis. The x direction defines the normal to the surfaces. In the presence of an applied electric field E the anisotropic contribution to the free energy density is given by

$$2F = K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n} + q_0)^2 + K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2 - \varepsilon(\mathbf{n} \cdot E)^2$$

where $q_0 = 2\pi/p_0$ is the undistorted wave vector and ε is the (positive) dielectric anisotropy including the vacuum permitivity. The director components are given by

$$n_x = \sin\phi(x, z), \quad n_y = \cos\phi(x, z), \quad n_z = 0 \tag{4}$$

and the boundary conditions $\phi(z > 0, x = \pm d/2) = +\pi/2$, $\phi(z < 0, x = \pm d/2)$

$= -\pi/2$ and $\phi(z = \pm\pi/2q, x) = \pm\pi/2$ where d is the cell thickness. Following Goossens we define

$$K_{11} = K_{33} = K, \gamma^2 = K_{22}/K, k = \gamma(d/2 - x). \tag{5}$$

The variable k is introduced for convenience in terms of obtaining a solution by conformal mapping in the complex plane. Since ϕ is an even function of x and an odd function of z we need to consider only $x, z \geqq 0$. The boundary conditions then become

$$\phi(k, z = \pi/2q) = \pi/2, \phi(k, z = 0) = 0\ \phi(k = 0, z) = \pi/2. \tag{6}$$

The jump of π at $z = \pm 0$, $k = 0$, implies the existence of a disclination which is necessary in order to sustain a properly defined two dimensional helical structure. For the fingerprint texture the actual occurrence of such a disclination is not established[17] and, for example, Press and Arrot claim that the lowest free energy configuration is free of disclinations.[4]

Goossens obtained an analytical expression for $\phi(k, z, q)$ by solving the two dimensional Laplace equation in z and k which results when one minimizes the free energy density in zero applied field. We have verified this result with the exception that it should be pointed out that it is exact only in the limit $\gamma qd/2 \to \infty$ (no boundary condition at $k = \gamma d/2$ has been specified). The resulting expression is:

$$\phi = \arctan[\tan(qz)/\tanh(qk)] \tag{7}$$

where

$$q = \left[2/\pi \int_0^{\pi/2} (\partial z/\partial\phi) d\phi\right]^{-1} \tag{8}$$

For finite $\gamma qd/2$ this solution has a non-physical discontinuity in $\partial\phi/\partial x$ at $x = 0$.

In the absence of an applied field the averaged free energy density is

$$F = \frac{4K_{22}}{\gamma dp} \int_a^{\gamma d/2} dk \int_a^{p/4} dz[(\partial\phi/\partial k)^2 + (q_0 - (\partial\phi/\partial z))^2] \tag{9}$$

where the lower limit a on both k and z has been introduced to avoid the singularity at $k = z = 0$. The variable parameter a is to be regarded as the radius of a cylindrical core giving the disclination mentioned previously. Evaluating the integral (9), using (7) for ϕ, we obtain

$$2F/K_{22} = (q - q_0)^2 - 2q \ln(2qa)/\gamma d. \tag{10}$$

Equation (10) is a corrected version of the expression given by Goossens. Minimization of the free energy with respect to q gives an implicit relation between q

and q_0 but the procedure depends on assumptions concerning the nature of the disclination. In order to satisfy the universality condition suggested by our data we have assumed that the core radius is proportional to the sample thickness i.e. that $a = cd$ where c is a constant. Geurst *et al.*[6] have shown that the radii of the $S = 1/2$ disclinations in twisted nematics are proportional to sample thickness (i.e. pitch). In our case we are led to a similar result even though we are dealing with a different geometry and boundary conditions. With the above assumption minimizing F with respect to q gives

$$q = q_0 + [1 + \ln(2qdc)]/\gamma d. \tag{11}$$

A plot of qd vs. $q_0 d$ is shown in Figure 4. The elastic free energy density for the homeotropic phase is given simply by

$$2F_H = K_{22} q_0^2. \tag{12}$$

Equating (10) and (12) we find that the transition to the homeotropic phase occurs at $qd^* = 2/\gamma$ as shown in the figure. For $qd < 2/\gamma$ the cholesteric phase is unstable relative to the homeotropic phase. From (11) we find that

$$(q_0 d)^* = (\beta d \Delta T)^* = [1 - \ln(4c/\gamma)]/\gamma \,. \tag{13}$$

4. The Free Energy Including the Applied Field

In order to obtain an expression for the critical voltage we make the further assumption that q is not coupled to the applied field E. That is, the applied field

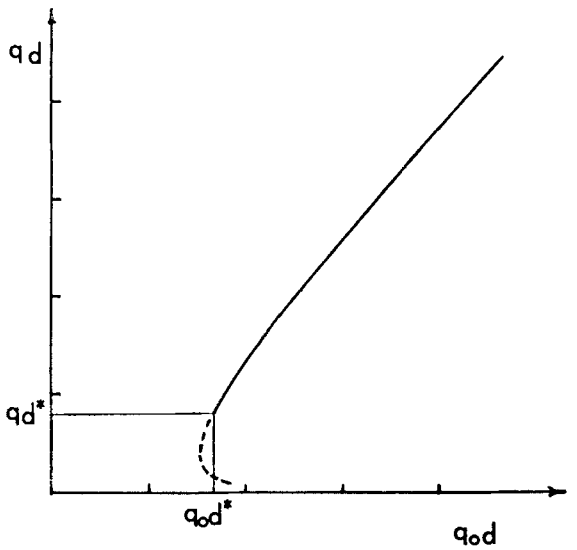

FIGURE 4 An illustrative plot of qd vs. $q_0 d$ as calculated from Equation (11). At the point $q_0 d^*$ the cholesteric phase becomes unstable relative to the homeotropic phase. Assumed values were $\gamma = 1$ and $a/d = 0.01$.

has a significant effect on q only in the region very close to the CH transition.[7] Hence we obtain the free energy for both cholesteric and homeotropic phases by simply adding a term quadratic in the applied field. For the cholesteric phase the free energy density is

$$2F_c = K_{22}[(q - q_0)^2 - 2q \ln(2qa)/\gamma d] + \varepsilon E^2[(e^{-\gamma qd} - 1)/2\gamma qd - 1/2] \quad (14)$$

and for the homeotropic phase we have

$$2F_H = K_{22}q_0^2 - \varepsilon E^2. \quad (15)$$

When $E = E_c$ we can equate Equations (14) and (15) which leads to the final expression for the critical voltage (using $V_c = E_c d$):

$$V_c = [2K_{22}qd(qd - 2/\gamma)[1 - (1 - e^{-\gamma dq})/\gamma qd]^{-1}]^{1/2}/\varepsilon^{1/2} \quad (16)$$

where q is given by (11).

DISCUSSION

Equation (16) above has been used for comparison with the data shown in Figure 3. For a given value of $c = a/d$, when $dq = 2/\gamma$, V_c drops suddenly to zero on the coexistence line. At this point, according to (13), $(\beta d\Delta T)^* =$ constant, thus confirming our experimental observations. Since the parameters in (16) are not accurately known for this mixture, we have chosen to obtain the nonlinear least squares best fit to the data shown on the universal curve. The parameters varied were K_{22}/ε, γ, and c. The solid curve in Figure 3 represents the best fit for which we calculate $K_{22}/\varepsilon = 0.079$, $\gamma = 1.19$, and $2c = 6.9 \times 10^{-3}$. These values seem quite reasonable for this mixture. Using the above values of c and γ, and Equation (11), we have calculated q vs. q_0 which is shown as the solid line in Figure 1. Using the known value of $\Delta\varepsilon = 7.7$ for pure 8CB we obtain an estimate of 5.4×10^{-12} N for K_{22}. The calculated value of c gives a core radius of 44 nm when $d = 12.7$ μm. This also compares favorably with the results of Geurst *et al.* who report a value of 30 nm, at the same thickness, for the disclinations in twisted nematics.[6]

Finally we consider the behavior of (16) in the de Gennes limit. For this comparison we consider the critical field E_c rather than V_c in the limit of infinite thickness. The ratio of the two equations in this limit is E_c (de Gennes)/E_c (Equation 16) $= (\pi/2)/2^{1/2} = 1.11$. The discrepency is due our assumption neglecting the effect of increasing field on q in the cholesteric phase.[7]

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