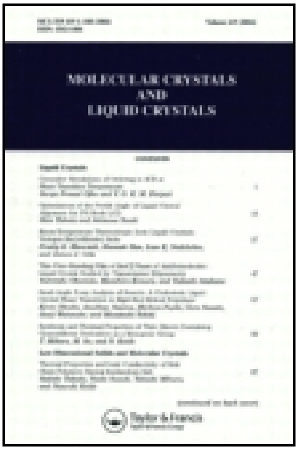

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Electric-Field Induced Phase Change in Cholesteric Liquid Crystals

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Abstract—Optically-negative cholesteric liquid-crystal films can be transformed to an optically-positive state by applying high d-c electric fields. A phase transformation occurs in which the helicoidal cholesteric structure is converted to either a planar smectic, or a linear nematic, structure. The threshhold field for this transformation has been studied as a function of sample thickness, temperature and composition. Bulk fields are responsible for the phenomenon. It is inferred that the compositional dependences are due to size factors and internal molecular dipole moments.

1. Introduction

Several workers have studied the effect of d.c. electric fields on cholesteric liquid-crystal films.[1–3] In these studies, the intensity of light reflected from cholesteric films was found to increase upon application of an electric field. Small changes in scattering wavelength were also found. Recently, we reported that a phase transformation could be induced in these films at high electric fields.[4] In these fields, the cholesteric molecules become aligned along the field direction, resulting in a uniaxial material with positive birefringence. Since cholesteric liquid crystals are ordinarily optically negative,[5] a phase transformation must have occurred to one of the two other liquid crystalline mesophases (smectic or nematic), both of which are optically positive.

The present work extends this observation of field-induced phase transformation. Its occurrence was examined as a function of sample thickness and composition. It will be shown that the transformation is caused by bulk fields and that packing factors play a role, as well as other parameters such as molecular dipole moments.

2. Experimental Procedure

A. Sample Preparation

Samples were prepared in the form of a capacitor with spacing determined by a mylar sheet. A hole, generally of triangular shape, was cut into the sheet to contain the liquid-crystalline film. The electrodes were glass cover-and-microscope slides onto which a transparent coating of chromium (optical density ≈ 0.15) was evaporated. The conducting face of the slides was placed in contact with the liquid crystal, and the resulting configuration was held together with epoxy. A diagram of the completed assembly is shown in Fig. 1.

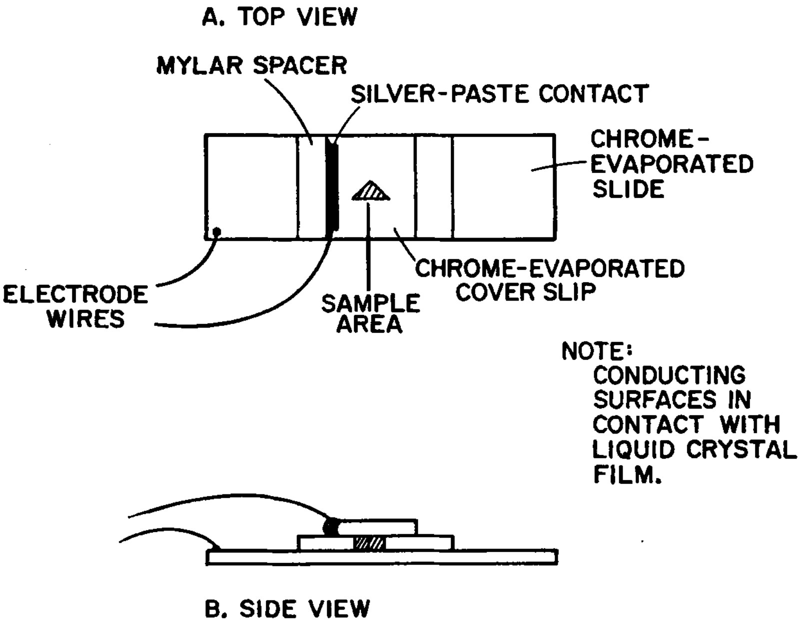

Figure 1. Sample configuration

B. MATERIAL SELECTION

Convenience and ease of handling were general considerations in material selection. Thus, in the study of thickness dependence, a mixture of cholesteryl chloride (CC), nonanoate (CN), and oleyl carbonate (COC) was used since it is stable in the liquid crystalline phase at room temperature. Easily obtainable materials were used in the study of compositional dependence. These materials frequently had liquid crystalline states which were supercooled at room temperature and were relatively unstable with respect to solidification. When these were used, measurements were made either in the supercooled state or at temperatures at which the cholesteric mesophase was stable.

TABLE 1 Cholesteric Materials Studied

Material	Symbol	Chemical Formula	Molecular Weight	Dipole Moment (Debye)	Manner in which studied
Chloride	CC	$C_{27}H_{45}Cl$	405.08	2.42(6)	Alone and mixed
Bromide	CB	$C_{27}H_{45}Br$	449.57	2.54(6)	Alone and mixed
Iodide	CI	$C_{27}H_{45}I$	496.54	—	Alone and mixed
Propionate	CP	$C_{27}H_{45}OCO(CH_2)_1CH_3$	442.73	2.23(6)	Mixed with CC
Hexanoate	CHx	$C_{27}H_{45}OCO(CH_2)_4CH_3$	484.81	—	Mixed with CC
Heptanoate	CHp	$C_{27}H_{45}OCO(CH_2)_5CH_3$	498.84	—	Mixed with CC
Nonanoate	CN	$C_{27}H_{45}OCO(CH_2)_7CH_3$	526.89	≈ 1(3)	Alone and Mixed
Dodecanoate	CD	$C_{27}H_{45}OCO(CH_2)_8CH_3$	568.97	—	Mixed with CC
Tetra-decanoate	CT	$C_{27}H_{45}OCO(CH_2)_{12}CH_3$	597.03	—	Mixed with CC
Palmitate	CPa	$C_{27}H_{45}OCO(CH_2)_{14}CH_3$	625.08	—	Mixed with CC
Stearate	CS	$C_{27}H_{45}OCO(CH_2)_{16}CH_3$	653.31	—	Mixed with CC
Oleate	CO	$C_{27}H_{45}OCO(CH_2)_7CH{:}CH(C_8H_{17})$	651.12	—	Alone
Oleyl Carbonate	COC	$C_{27}H_{45}OCOO(CH_2)_8CH{:}CH(CH_2)_7CH_3$	681.41	—	Alone and Mixed

The materials which were examined in this study, either alone or mixed with other cholesteric compounds, are listed in Table 1. The abbreviations used in this text for the compounds are listed together with the chemical formula, molecular weight, and dipole moment of the compounds and the manner in which they were used. Although values of dipole moment were unavailable for all of the listed materials, it is inferred that the value is 1 to 3 debye for the entire group. The direction of the dipole moment is presumed to be along the axis of the molecule for the organic halides and at an angle to it for the esters. Chain length L in the esters is the number of CH_2 groups occurring in the chain; for example $L = 8$ in CD.

The materials were usually used as purchased without any attempt to purify them. In one experiment, however, CC and CN components were both recrystallized 5 times from an ethyl alcohol solution. Differential thermal analyses of the material before and after crystallization showed almost no change. It seems reasonable to conclude therefore that original material purity of at least some of the compounds was sufficiently high not to be improved significantly by five recrystallizations. As corroboration of this hypothesis, no significant difference in electrical behavior was observed in samples made from original and purified material.

C. METHOD OF INDUCING AND MEASURING PHASE TRANSFORMATION

The sample was put on a hot-stage of a Leitz Ortholux polarizing microscope. Measurements were made in the transmission mode with convergent white light, a 50 × objective, crossed polarizers, a first-order-red gypsum plate and a Bertrand lens. Before application of voltage, the material was birefringent, and usually consisted of irregular blue and yellow regions separated by irregular pink lines when viewed between crossed polars with the gypsum plate. This texture has been referred to as the focal-conic texture.[7] There was usually no evidence of alignment in the direction of light propagation. Occasionally, however, some alignment was present, or, if not, it could be induced by mechanically displacing the upper electrode in a shearing mode. In this case, a uniaxial isogyre could be obtained when the sample was viewed through the Bertrand lens. The optical sign was established from the color figure resulting when the gypsum plate was inserted,[8] which in this case consisted of yellow in the 1st and 3rd quadrants and blue in the 2nd and 4th. This pattern is associated with negative birefringence, a well-known characteristic of the cholesteric mesophase.[5] When small fields were applied, this alignment was destroyed and the irregular blue and yellow areas appeared when viewed with the gypsum plate. As the field was increased, these areas broke up into thread-like lines, the threads ordinarily consisting of closed loops. At still higher fields, the threads disappeared; the field now was black between crossed polars. Insertion of the Bertrand lens led to an isogyre signifying the uniaxial nature of the material. Quite significantly, the color figure associated with the isogyre was blue in the 1st and 3rd quadrants and yellow in the 2nd and 4th. This color pattern is characteristic of optically-positive material. Thus, a phase change must have been induced by the field. Since positive birefringence is associated only with nematic and smectic mesophases, the transition[4] was from the cholesteric to either the nematic or smectic mesophase, but most probably to the nematic form in view of the thread-like nature of the material just prior to the transformation. (A cholesteric-nematic transformation induced by magnetic fields was recently reported.[9]) It should be pointed out that none of the alignment or color figures noted for either the cholesteric or the transformed phase changed when the hot stage was rotated.

Near threshold, the field of view never completely converted to the optically-positive state at one voltage, but rather over a narrow range of voltages. It was arbitrarily decided to define the threshold voltage as that at which the entire field first became dark between crossed polars. Because of this, the threshold voltage quoted here is frequently 5–10% above the value at which the transformation began.

Several minutes were allowed at each voltage setting in the vicinity of threshold to allow an equilibrium to occur. This delay was necessary because material movement was obviously involved in the transformation. Since the viscosity of the material is not negligible ($\approx$ 100 cP.), movement at the threshold was slow and had to be taken into account to insure reasonably accurate threshold data.

When the field was decreased after the transformation had occurred, the material reconverted to a birefringent, cholesteric state similar to that before the transformation. Noticeable misalignment occurred when the field was decreased only slightly below threshold value. The voltage at which misalignment first started was not studied in detail; it is felt, however, that it represents a small hysteresis, if indeed any exists at all.

The threshold field was obtained by dividing the threshold voltage by sample thickness. The thickness was obtained with the microscope by measuring the distance the stage had to be moved vertically to focus on imperfections in the top and bottom electrodes. Refractive effects were compensated by immersing the lens in an oil which matched the refractive index of the liquid crystal, taken as 1.49.[10] Cotton-seed oil with an index of 1.47 was used. The suitability of cotton-seed oil was checked by comparing thickness measurements made with oil in areas containing liquid crystal to those made without oil in bubble areas devoid of material. The ratio of these thickness values averaged 0·98, indicating the index of cotton-seed oil is indeed a good match to that of the liquid crystal. The thickness was measured with a voltage applied comparable to the threshold voltage to insure that it was the value corresponding to the threshold field. Despite all precautions, however, the thickness measurement was difficult to perform accurately, primarily because of the problem of identifying unambiguously imperfections at the top and bottom of the sample. Accuracy of measurement is thus no better than 20% which results in a similar inaccuracy in threshold field.

Temperature measurements were made on each sample using a chromel-alumel thermocouple attached to the upper electrode. The couple was placed as close to the sample area as possible, consistent with the presence of the objective. Regardless, temperatures measured in this way were uncertain by 2–4 °C, primarily because of the proximity of a relatively cold objective lens to a warm sample. Maximum uncertainty in sample temperature is considered to be 10%. Thus slopes of field *vs.* temperature shown below have inaccuracies up to 30%.

Sample current was monitored throughout the measurements. Samples generally had current densities below 10^{-7} A/cm^2, typically 10^{-9} A for the active sample areas used. Exact values of current density were not established because of the problem of noise in the spread-out, high-impedance circuitry. Furthermore, the exact value of current density was not required to establish threshold behavior, providing it was below 10^{-7} A/cm^2.

D. Pressure Effects

Because of the known sensitivity of liquid crystals to pressure, itwas necessary to exclude this effect as a possible cause of the phase transformation. The force of attraction between the electrodes, for example, is computed to be 2.7 newtons (0.6 lbs) for an applied voltage of 400 V, a 6μ spacing, a dielectric constant of 3, and a total sample area of 4 cm^2. Thus, it might be argued that pressure due to this force was partially responsible for the transformation. Attempts to achieve transformation to an optically-positive state by simply pressing the sample with a force this great or even greater, however, were unsuccessful.

Further confirmations that squeezing does not play a significant role were obtained in the following two experiments. In the first, the threshold voltage was established and then reduced by 2%. The phase transformation ceased. The sample was then squeezed, with the reduced voltage applied, to the point at which the top cover glass broke. No sign of a phase change was observed. In the second, samples were prepared with a compound mylar spacer in which holes of different size were cut. The mechanical force on material in the vicinity of that in the common hole areas is very nearly the same because of the electrode rigidity. Yet, at threshold, the phase transformation occurred only in the common hole area. Thus, electrical, rather than simple mechanical, forces must be involved in the phase transformation.

3. Results

A. THRESHOLD *vs.* SAMPLE THICKNESS

The initial experiments were performed to establish whether the phase transformation is due to bulk or to surface-dependent phenomena. Toward this goal, the threshold voltage was determined as a function of temperature for a mixture of 30% (by weight) CC, 56% CN and 14% COC. Samples were constructed whose spacing *t* varied from 15 to 114μ. An example of data

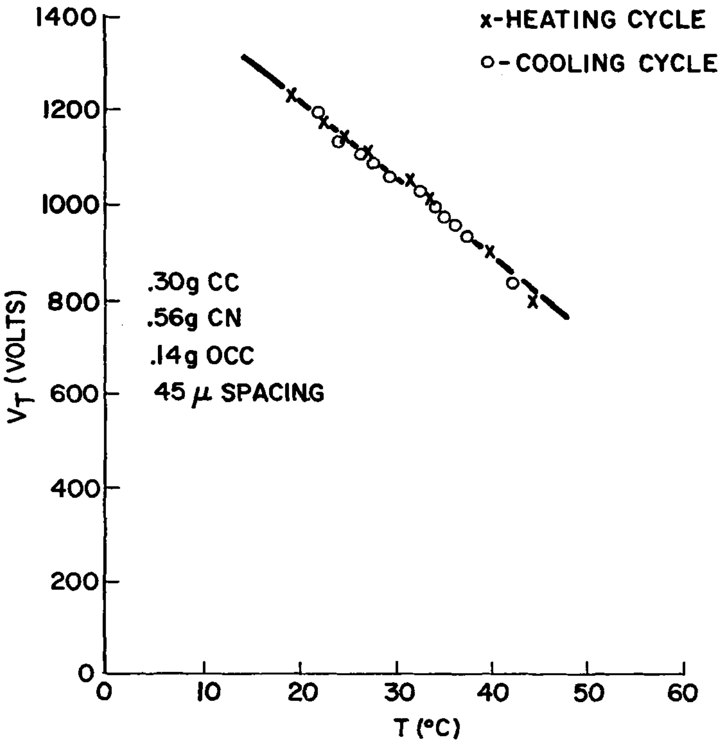

Figure 2. Threshold voltage *vs.* sample temperature

obtained is shown in Fig. 2 where threshold voltage V_T is plotted against temperature T. Data obtained for both increasing and decreasing temperatures indicate there is no temperature hysteresis. The threshold voltage decreases linearly with T in the temperature range shown. Beyond 50 °C, break away from linearity occurs indicating approach to the isotropic transition temperature, which is $\approx 57\,°\mathrm{C}$ for this material. For lower temperatures, the data can be well characterized by an intercept and a slope.

The intercept is here taken as the value of threshold at 21 °C.

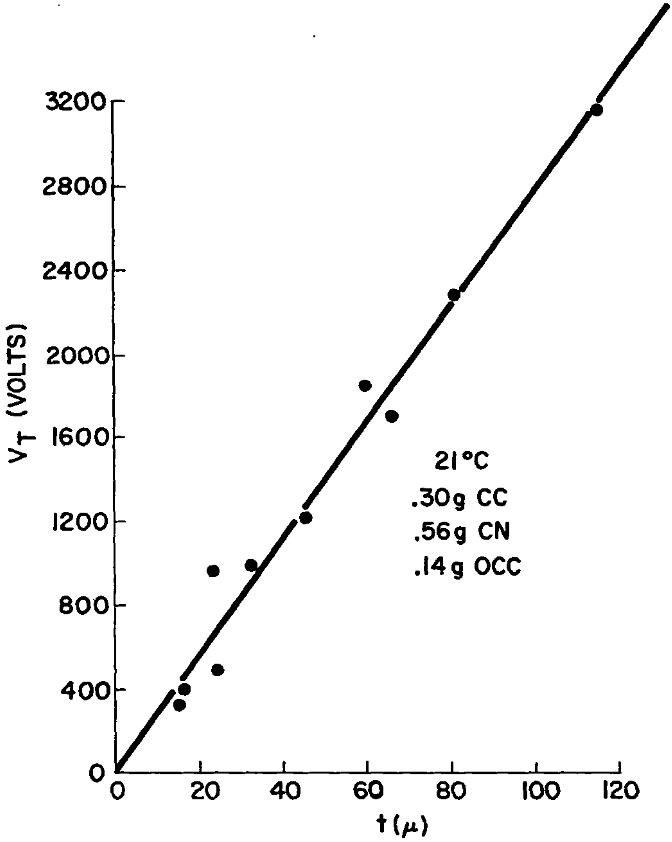

Figure 3. Threshold voltage *vs.* sample spacing

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It is shown in Fig. 3 as a function of sample spacing *t*. A good representation for the data is a straight line which passes through the origin, indicating that the observed phenomenon must be due to a bulk field and not to surface-connected influences. If the latter were present, the line would not have a zero intercept because at small spacings, the surface would be expected to dominate. The bulk field required for the transformation in this material is 2.8×10^5 V/cm at 21 °C.

Further corroboration of this conclusion is shown in Fig. 4 where the slope m_v of the threshold-temperature data is plotted against *t*. For convenience in plotting, m_v has been multiplied by -1. Linear behavior with an intercept through the origin is

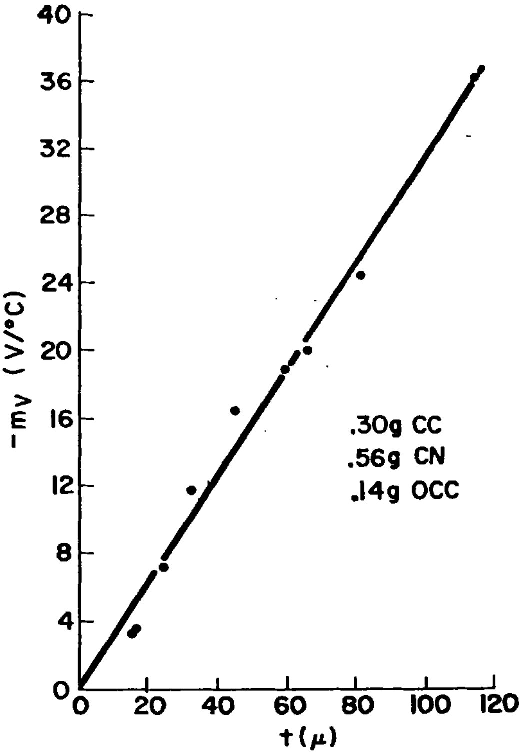

Figure 4. Slope of threshold voltages with temperature *vs.* sample spacing.

noted. This again is the behavior expected if bulk fields, and not surface phenomena are dominant,. In terms of field, the slope can be expressed as 3.1 × 10^3 V/cm °C for this material. An analytical expression for the threshold field E_T in this material is thus

$$E_T = 2.8 \times 10^5 - 3.1 \times 10^3(T - 21). \tag{1}$$

Equation (1) does not hold of course in the vicinity of the isotropic-transition temperature.

It is concluded from this study that the phase change is due to bulk fields. The magnitudes of these fields are temperature dependent in this material; i.e. threshold field decreases with increasing temperature.

B. Dependence of Threshold on Composition

A variety of mixtures and compositions were studied to shed light on the phase change. The basic constituents are listed in Table 1. It was soon found that the phase change could be easily obtained only when a halide such as CC, CB, or Cl was present. Whenever the halide was absent, dielectric breakdown of the sample occurred before the phase transformation. Thus, it was not possible to achieve the phase change in samples made with CN, COC, CO or a mixture of COC and CN. An alignment was observed in CN, but only to the characteristic state of the cholesteric mesophase; i.e. an optically-negative state. Use of a halide, solely or in mixture with any other of the compounds listed in Table 1, made the phase transformation easily achievable.

Given this result, the phase change was studied as a function of composition first in a system consisting of various proportions of CC and CN and then in a system consisting of a 1 : 1 molecular composition of CC and cholesteric esters of various chain lengths.

Figure 5 shows the threshold field E_T at 21 °C for various mole percentages β of CC in (CC + CN) mixtures. Also given is the weight percentage α of CC in these mixtures. The value of E_T decreases sharply as CC is added to the system, reaching a minimum at $\approx$ 70 mole % CC and subsequently rising slightly to a

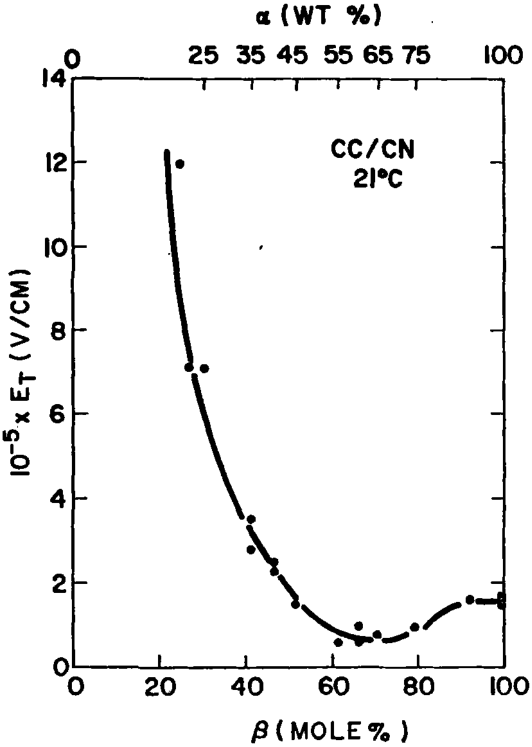

Figure 5. Threshold field *vs.* molecular percentage of chloride in chloride/nonanoate mixtures.

plateau independent of β at high CC concentrations. Similar behavior was seen in the slope m_E of the threshold field *vs.* T as shown in Fig. 6. For convenience in plotting, the value of m_E has been multiplied by -1. At large values of β, m_E was zero; that is, the threshold field was independent of T below the isotropic transition temperature.

Data in Fig. 5 is consistent with the observation that the phase transformation is difficult to achieve when CN is used alone. It is apparent that fields much greater than 10^6V/cm would be required to achieve the phase transformation in CN. None of the samples could withstand such fields before dielectric breakdown.

The effect of ester chain length L in a 50 mole % mixture of CC

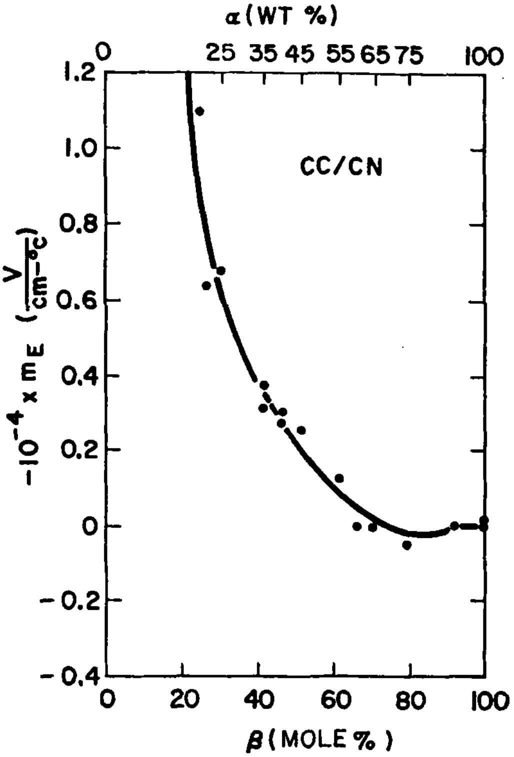

Figure 6. Slope of threshold field with temperature *vs.* molecular percentage of chloride in chloride/nonanoate mixtures.

and cholesteric ester was investigated next to assess the effect of steric factors on E_T. Data of E_T at 21 °C and m_E are shown in Figs. 7 and 8, respectively. Again m_E has been multiplied by -1 for convenience in plotting. Both E_T and m_E are seen to depend linearily upon L. Longer chains require higher fields which then decrease faster with T than fields associated with smaller-chain esters. Not shown in Figs. 7 and 8 are the results obtained with a mixture CC and CS. It was not possible here to obtain a mesomorphic phase sufficiently stable to allow measurements to be made.

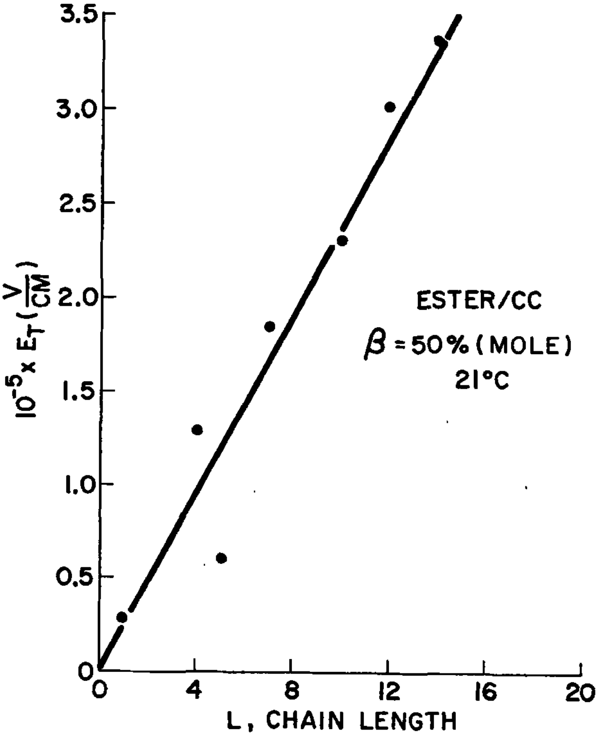

Figure 7. Threshold field *vs.* chain length of ester in ester/chloride mixtures.

4. Discussion of Results

Matters for discussion are the existence of a threshold and the effects of temperature and composition on the threshold. The phase transformation is conceived to occur in the following fashion starting with an aligned cholesteric state. In this initial state, the optic axis of the material is perpendicular to the electrodes. Thus, the molecules themselves are in planes parallel to the electrodes, a configuration in which it is easy to observe the characteristic negative optical sign of the material. When a field of low intensity is applied, torques exerted on the molecules because of dipole interaction, if properly directed, twist them so that their planes are now parallel to the field; as a result, the optic axis of the cholesteric structure is perpendicular to the field.

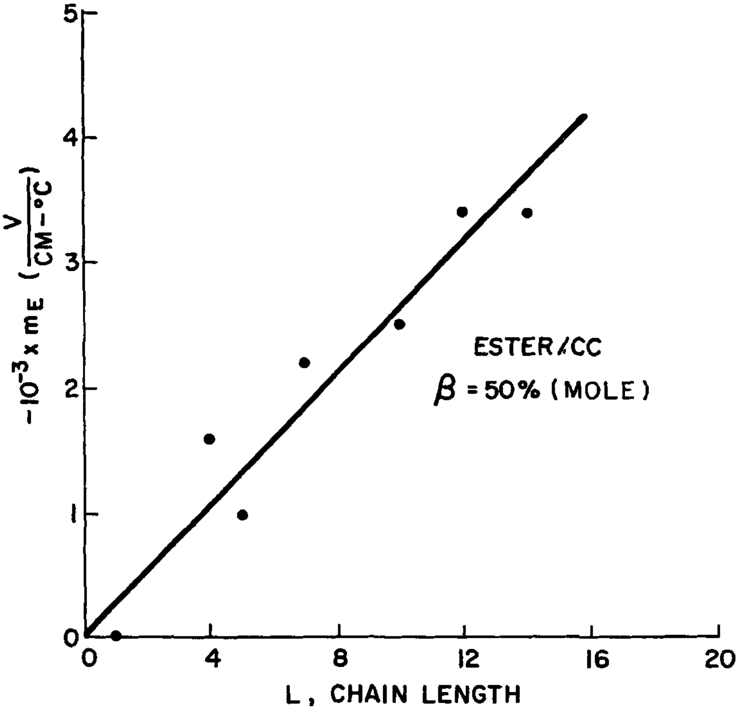

Figure 8. Slope of threshold field with temperature *vs.* chain length of ester in ester/chloride mixture.

The material appears birefringent and has a texture such as described previously.[7] It is presumed of course, that the helicoidal structure exists whether or not the optic axis is parallel or perpendicular to the electrodes.

This suggested behavior presumes that a major component of dipole moment lies along the molecular axis. Otherwise it is difficult to see why low-intensity fields should disrupt the initial alignment. In the case of the compounds and mixtures containing very little of the organic halide, however, the component along the axis is postulated to be small in accordance with the experimental difficulty of affecting these materials with fields.

As the field is increased, the helicoidal structure is disrupted and all of the molecules become aligned parallel to the field, which corresponds to the phase transformation displaying the optically-positive sign. The interaction is again between the field and dipole moment. It is apparent, however, that forces of electrical and mechanical nature oppose the transformation, and it is only when they are overcome by the bulk threshold field that the transformation is achieved. Internal electrical forces are those between molecules within a plane and with those in adjacent planes while mechanical forces are friction and packing-type forces arising from size effects and the non-planar nature of the molecules. These internal forces are very sensitive to the distance of the molecules from each other.[11] It is not possible to describe these forces well qualitatively, much less quantitatively. Their magnitude must however be that of the threshold field times an effective dipole charge; the threshold field thus provides a measure of the internal molecular environment. The decrease in threshold field with temperature, when observed, signifies a reduction of the internal forces, possibly because of small increases in molecular separation and increased thermal vibrations.

Before further interpretation of the data is possible, our knowledge of the internal environment of the cholesteric structure must be advanced. It must be determined, for example, how constituents of a mixture combine in all proportions to form material whose properties are so uniform and regular that their optical properties can be described and specified to high precision.[12] When such matters are clarified, data presented here can be related to the nature and configuration of the cholesteric structure without much ambiguity.

5. Conclusion

Bulk electric fields applied to cholesteric mixtures convert the optically-negative material to aligned, optically-positive material. The threshold field is a function both of temperature and mixture composition. Compositions with little or no halide (such as cholesteryl chloride) require such high fields for the phase transformation that sample breakdown invariably occurs beforehand.

When halide is present, the ester chain length then significantly affects the magnitude of threshold field. Longer chain lengths lead to higher threshold fields. It is presumed that the phase transformation occurs because of forces arising between the field and molecular dipole moments. Internal forces of electrical and mechanical nature evidently oppose the transition.

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