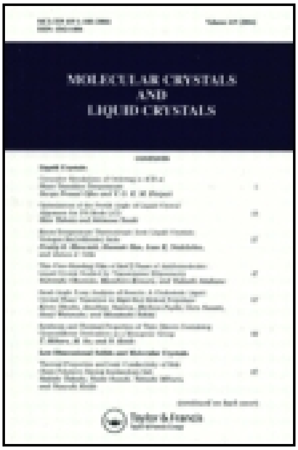

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Anisotropy Changes in the Cholesteric to Nematic Phase Transition

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Anisotropy Changes in the Cholesteric to Nematic Phase Transition

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It is well known that solutions of cholesteric compounds in negative nematics can be switched reversibly between a "clear" state and a "scattering" state by electric fields of suitable amplitude and frequency. Both states are stable for suitably chosen composition and ε and σ can be measured for each state without disturbing the state. It is found that $\varepsilon_s < \varepsilon_c$ and $\sigma_s > \sigma_c$ for the low frequency region. The anisotropy $\Delta\varepsilon = \varepsilon_s - \varepsilon_c$ is independent of the cholesteric concentration and about equal to one-half of $\Delta\varepsilon$ of the nematic solvent. The in-phase term consists of two parts describing carrier transfer, $\sigma(0)$, and dielectric loss $\sigma(v)$. The maximum frequency for transfer from clear to scattering depends on $\sigma(0)$ and is approximately given by the Debye relaxation frequency. The turn off frequency is always larger than the Debye relaxation frequency but smaller than the dielectric relaxation frequency. The clear state is identified with parallel alignment. The scattering is regarded as Raleigh scattering from well aligned regions randomly oriented throughout the bulk of the liquid.

INTRODUCTION

The anisotropy of the permittivity (ε) and the conductivity (σ) of a purely nematic liquid crystal is conveniently determined by measuring the capacitance and conductance of a test cell held in a magnetic field either parallel with or perpendicular to the direction of the electric field.[1,2] For m.b.b.a. and other negative nematics it is found that

$$\varepsilon_{\parallel} < \varepsilon_{\perp} \quad \text{and} \quad \sigma_{\parallel} > \sigma_{\perp}.$$

Thus if the alignment of the molecular axis is parallel with the electrode surface the experiment yields the larger of the two polarizations (H ⊥ E). The external magnetic field required for these measurements is relatively modest Initially the anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ increases wlth the H field but eventually $\Delta\varepsilon$ reaches a constant value in the 5–10 kGauss region.

Dilute solutions of a cholesteric compound in a nematic can be aligned in a magnetic field much as the solvent itself. For more concentrated solutions, above about 5 %, magnetic fields of the order of 10 kGauss can no longer affect the alignment although transitions have been observed with N.M.R. fields, of the order of 100 kGauss.[3]

The low concentration region, 0.1 to 2 % was studied by Rondelez and Hulin.[4,5] Starting from a planar aligned cholesteric phase, a magnetic field perpendicular to the electrode surface eventually turns the sample nematic with at least the solvent aligned perpendicular to the surface. The accompanying decrease in the cell capacitance is plotted as a function of the magnetic field but unfortunately the authors do not calculate $\Delta\varepsilon$ and $\Delta\sigma$.

For the high concentration region, where magnetic fields no longer produce switching, one can use the storage properties to determine the anisotropy. It is now well known[6,7] that such solutions can be switched from the initially clear state to a scattering state by a low frequency sine wave. The scattering state persists after the signal has been removed. A higher frequency signal of sufficient amplitude will bring the sample back to a clear state and again the sample will remain clear after the generator has been turned off.

The permittivity and conductivity of the clear and the scattering states can be measured on the same sample since the field required for the electrical measurement is much smaller than that required for switching. In the following it is shown that

$$\varepsilon_s < \varepsilon_c \quad \text{and} \quad \sigma_s > \sigma_c$$

for the low frequency region. The subscripts "s" and "c" refer, of course, to "scattering" and "clear." A newly filled cell shows parallel alignment. If the cell is cycled repeatedly finally ending with the clear state it is found that the clear state is electrically and optically indistinguishable from the initial state. Thus it is reasonable to identify ε_c with parallel alignment. As the concentration of the cholesteric compound is increased ε_c and ε_s both decrease but the magnitude of the anisotropy $\Delta\varepsilon = \varepsilon_c - \varepsilon_s$ remains constant and equal to one-half of the anisotropy of the solvent. This can be accounted for only by random distribution of the dipole moments. However to account for the strong light scattering there must be fluctuations in the index of refraction over distances of a few wavelengths. Combining the two requisites the liquid in the scattering state is thought to consist of well aligned regions of the order of microns distributed in random orientation throughout the liquid. This model is verified by polarization microscopy.

It is of interest to study the switching mechanism and the change in light scattering after the low frequency field has been turned off. The frequency of the drive sine wave can be changed from a few Hertz to nearly 1000 Hz by adding suitable dopants. It is shown that there is a correspondence between the Debye relaxation frequency and the turn on frequency. The turn off frequency is always much larger than the space charge relaxation frequency but it is smaller than the dipole relaxation frequency.

EXPERIMENTAL PROCEDURES

A bridge circuit suitable for measuring ε and σ of liquid crystal samples throughout the audio range (0–20 kHz) has been described.[8] Whenever it was necessary to extend the measurements to higher frequency a Boonton bridge 5–500 kHz was used.

Test cells are made by sputtering about 1000 Å of indium/tin oxide on 1 × 2″ glass plates and etching a 0.5″ circle which forms the electrode. A 0.01″ line connects the electrode to an external contact. Two plates separated by 0.0005″ mylar spacers are lined up and bonded together. The cell constant is obtained from the capacitance of the empty cell. These cells operate well in the audio range but tend to become lossy beyond 100 kHz probably by surface leakage. However it is more important to have reproducible surface conditions. Plates are cleaned and dried rigorously and used only once. All mechanical assembling is done in dry N_2 atmosphere. Test cells are mounted in an enclosure continuously flushed with dry nitrogen.

The solvent, m.b.b.a. (Kodak) was recrystallized twice from isopropanol at 3°C, residual alcohol was removed in a vacuum rotary evaporator. The resistivity of the end product is usually larger than 10^{11} ohm-cm. During the course of this work Kodak-refined m.b.b.a. became available. Presumably this could have been used without additional purification.

RESULTS

Conductivity and Dielectric Loss

Table I lists the permittivity and the conductivity for a sample of 12% cholesteryl oleyl carbonate in m.b.b.a. for three conditions: (*a*) as filled, (*b*) after being brought into the scattering state by a 10 Hz 40 Vrms sine wave and, finally, (*c*) in the clear state after repeated cycling between the low frequency sine wave and a 700 Hz 40 V sine wave. The data are reproduced here to indicate that the "as filled" state is identical to the clear state. Microscopic examination leads to the same conclusion. Table I indicates that:

$$\varepsilon_s < \varepsilon_c \quad \text{and} \quad \sigma_s > \sigma_c.$$

In this frequency range ε is constant but σ increases with frequency. In Figure 1 the frequency range is extended to beyond 100 kHz. The figure

TABLE I

Permittivity and Conductivity of a 12% Cholesteryl Oleyl Carbonate Solution in m.b.b.a.

Hz	As filled		Scattering		Clear	
	ε'	$\sigma \times 10^{-11}$	ε'	$\sigma \times 10^{-11}$	ε'	$\sigma \times 10^{-11}$
10	4.68	1.16	4.60	1.21	4.68	1.16
20	4.73	1.16	4.56	1.21	4.73	1.23
50	4.69	1.16	4.53	1.36	4.70	1.11
100	4.66	1.16	4.53	1.25	4.65	1.16
200	4.64	1.16	4.53	1.45	4.65	1.21
500	4.72	2.25	4.53	2.58	4.65	2.36
1000	4.65	4.95	4.52	5.29	4.60	5.10
2000	4.59	22.0	4.47	22.1	—	—
	$\bar{\varepsilon} = 4.66$		$\bar{\varepsilon}_s = 4.54$		$\bar{\varepsilon}_c = 4.66$	

indicates the conductivity for (*a*) the solvent in parallel and perpendicular alignment, (*b*) two solutions of cholesteryl oleyl carbonate showing σ_s and σ_c and (*c*) a 11% cholesteryl oleyl carbonate solution doped with 0.5% Hyamine 10.

The $\sigma(\nu)$ curves for all solutions tend to converge to the curve for the solvent. Therefore the increase is not caused by a conduction mechanism but rather by a dielectric loss mechanism common to solvent and solution. If C is the capacitance of the filled cell, C_0 that of the empty cell and ε^* the complex permittivity, one has in the usual way:

$$C = \varepsilon^* C_0 = \varepsilon' C_0 - j\varepsilon'' C_0. \tag{1}$$

The current through the cell arm is:

$$I = \left(\frac{1}{R} + \omega\varepsilon'' C_0 + j\omega\varepsilon' C_0\right)V. \tag{2}$$

And, since the bridge equates the cell with a parallel R, C network, the in-phase component is:

$$\frac{1}{R} + \omega\varepsilon'' C_0 = \frac{1}{R_m} \tag{3}$$

and the out-of-phase part is

$$\varepsilon' C_0 = C_m \tag{4}$$

where the index m refers to the standard arm. The d.c. conductivity is obtained from:

$$\frac{1}{R} = \sigma \frac{C_0}{\varepsilon_o} \tag{5}$$

where $\varepsilon_o = 8.854 \times 10^{-14}$ F cm^{-1}.

By analogy, let:

$$\frac{1}{R_m} = \sigma(\nu)\frac{C_0}{\varepsilon_o} \tag{6}$$

and thus formally:

$$\sigma(\nu) = \sigma(0) + \omega\varepsilon_o\,\varepsilon''. \tag{7}$$

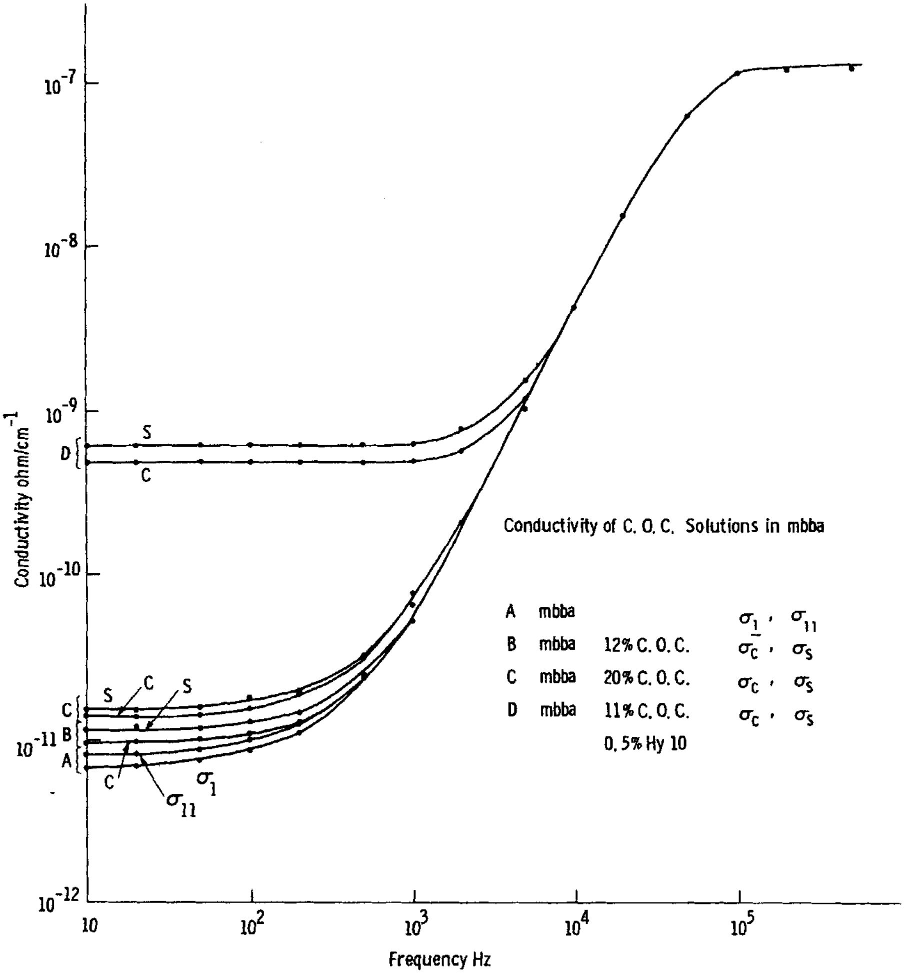


FIGURE 1 Real part of the cell impedance as function of frequency.
Curves A solvent, m.b.b.a. in parallel and perpendicular alignment
Curves B 12% solution of cholesteryl oleyl carbonate in scattering and clear state
Curves C as B but for a 20% solution
Cuves D an 11% solution of cholesteryl oleyl carbonate to which 0.5% Hyamine 10 is added to provide conductivity.

Figure 1 illustrates the magnitudes of the two terms $\sigma(0)$ and $\omega\varepsilon_o\varepsilon''$. For an undoped solution $\sigma(0)$ is small and the effect of the loss term $\omega\varepsilon_o\varepsilon''$ is noticeable at low frequency, even at 100 Hz. If a dopant is added to increase $\sigma(0)$ to e.g. 10^{-9} (ohm cm)$^{-1}$ the effect of the loss term is noticeable only at high frequency, beyond 5 kHz in this example. For any sample the low frequency conductivity of the scattering state is always larger than that of the clear state, whether or not the sample is deliberately doped. But for all samples the $\sigma(\nu)$ curves eventually coincide with the curve for the solvent.

The low frequency conductivity is a charge carrier transport mechanism. It depends on the dopant concentration in accordance with the Onsager-Fuoss theory.[8]

In Figure 2 the real part ε', and the imaginary part ε'', of the permittivity are plotted versus frequency for m.b.b.a. and for a 10% cholesteryl oleyl carbonate solution. The loss curve is reminiscent of dielectric relaxation except that $\varepsilon''_{\text{max}}$ occurs at much lower frequency than normally observed for dipole relaxation. The ε'' curves for solvent and solution differ slightly but for both the relaxation time is of the order of 3 microseconds while true dipole relaxation times are of the order of a nanosecond. Meier and Saupe[9] discussed dielectric loss for a number of alkoxy azoxy benzenes. Dielectric

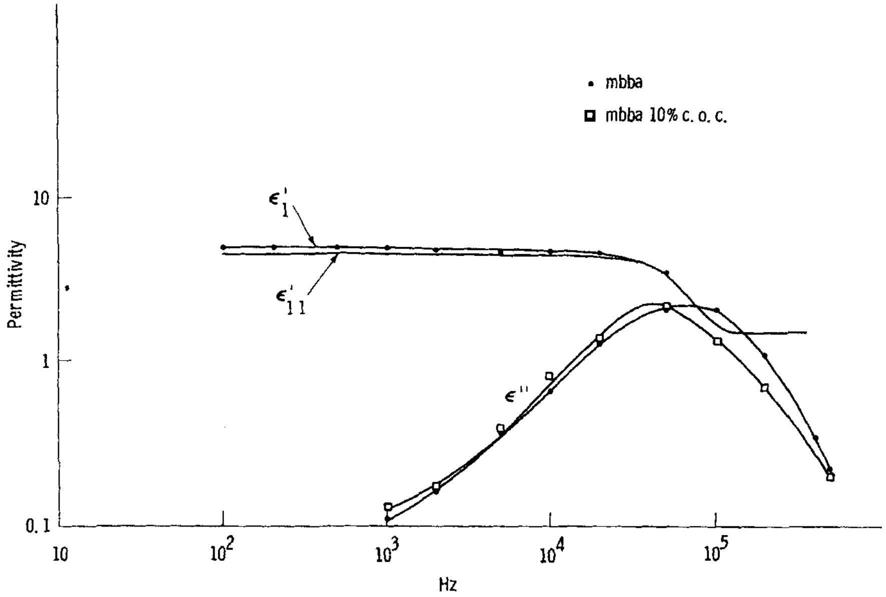


FIGURE 2 Real and imaginary part of the permittivity for m.b.b.a. and for a 10% solution of cholesteryl oleyl carbonate. Between 1 and 10 kHz the loss curve for $\varepsilon''_s < \varepsilon''_c$ but near the relaxation frequency both curves merge together. This detail was omitted to simplify the figure.

absorption occurs in the 100 kHz region comparable to our results, but it is only the parallel component of the polarization which shows relaxation at these low frequencies. Maier and Meier[10] associated the loss mechanism with hindered rotation around the perpendicular axis. For cholesteric-nematic solutions, as is clear from Figure 2, the dielectric loss does not differ for the scattering or the clear sample and since certainly the clear sample is parallel aligned it is the perpendicular component of the polarization which shows low frequency relaxation. Baessler, Beard and Labes[11] found relaxation times of the order of 500 microseconds for mixtures of cholesteryl esters. Referring again to Figure 2, it is seen that the anisotropy of the real part of the permittivity can be determined only at frequencies well below the relaxation frequency.

Low Frequency Anisotropy of Cholesteric Solutions

Table II lists the real part of the permittivity for m.b.b.a. and cholesteryl oleyl carbonate solutions for frequencies below 1 kHz. $\varepsilon_\perp$ is the permittivity of the solvent, ε_c that of the solutions, aligned essentially parallel with the electrode surface. $\varepsilon_\parallel$ is the permittivity of the solvent in perpendicular alignment and ε_s is the permittivity of the solutions in the scattering state. For dilute solutions ε_s cannot be measured because the scattering state does not persist long enough but for sufficiently concentrated solutions the scattering state is stable and reproducible data can be obtained.

TABLE II

Permittivity (Real Part) of Cholesteryl Oleyl Carbonate Solution

m.b.b.a.	$\varepsilon_\perp$	4.98	$\varepsilon_\parallel$	4.73	$\Delta\varepsilon$	0.25
4.95% COC	ε_s	4.81	—	—	—	—
9.63% COC	ε_s	4.66	ε_s	4.57	$\Delta\varepsilon$	0.09[a]
11.96% COC	ε_c	4.66	ε_s	4.54	$\Delta\varepsilon$	0.12
15.06% COC	ε_c	4.64	ε_s	4.52	$\Delta\varepsilon$	0.12
20.2% COC	ε_c	4.49	ε_s	4.37	$\Delta\varepsilon$	0.12

[a] Storage time insufficient for precise measurement.

The anisotropy $\Delta\varepsilon = \varepsilon_s - \varepsilon_c$ is about one-half of that of the solvent. Therefore the scattering state cannot represent perpendicular alignment of solvent and solute molecules. Since the polarization is mainly that of the solvent, this result indicates random distribution of the dipole moments. However since a homogeneously random solution would not cause strong light scattering we assume that in the scattering state the liquid consists of small regions, well aligned internally but randomly distributed throughout the bulk. This model is readily confirmed by examination under the polarization microscope.

Figure 3 was made from a series of 35 mm color slides, taken at 160X magnification, crossed polarizers and a quartz wedge compensator adjusted for maximum color contrast. The photographs form a time sequence and for convenience a solution was prepared having approximately 10 minutes of storage. A sample in the clear state, as filled, appears uniformly homogeneous. Dislocation loops typical of nematic solutions are absent. Figure 3a shows the scattering state immediately after the field has been turned off. The liquid contains many small ordered regions randomly dispersed. In time the ordered regions increase in size and appear to be cholesteric (Figure 3b) until finally the ordered regions occupy nearly all of the liquid as in Figure 3c. A texture such as Figure 3b still scatters but a texture as Figure 3c scatters very weakly. If a high frequency field is applied to a sample in a scattering state, the regions such as Figures 3a or 3b become aligned, dislocation loops disappear and the liquid is homogeneous in texture as in Figure 3d.

Storage Time

For all solutions studied, the size of the ordered regions increases and therefore the intensity of the scattered light decreases after the low frequency field has been turned off. However the rate of growth differs greatly between solutions of different concentration and between different solutes. Thus by doubling the concentration of the Schiff's base used in Figure 3 the storage time becomes many hours. For a 20% solution of cholesteryl oleyl carbonate the storage time is many months. The decay of the scattered intensity is determined conveniently by equipping the polarization microscope with a photo diode and plotting the relative intensity of the scattered light versus time. Figure 4 illustrates representative results. In each photograph the upper trace represents the applied voltage, the lower trace is the photo diode output. The time period between turn on and turn off was set at one hour.

The photographs show the effects of concentration and the result of adding dopants. The rate of change of the scattered intensity is largest immediately after the field is turned off. This correlation with the change is size of the scattering centers. By adding dopants the frequency at which the cell can be turned on is increased.

DISCUSSION

Reversible switching beween a scattering and a clear state is observed only if the dielectric anisotropy of the solution is negative as for example cholesteryl fatty esters or (—) 2-methylbutyl-*p*-(4-methoxybenzylidene)amino cinnamate dissolved in m.b.b.a. If the cholesteryl ester is positive as for example cholesteryl chloride or if the methoxy group in the cinnamate is replaced by cyano

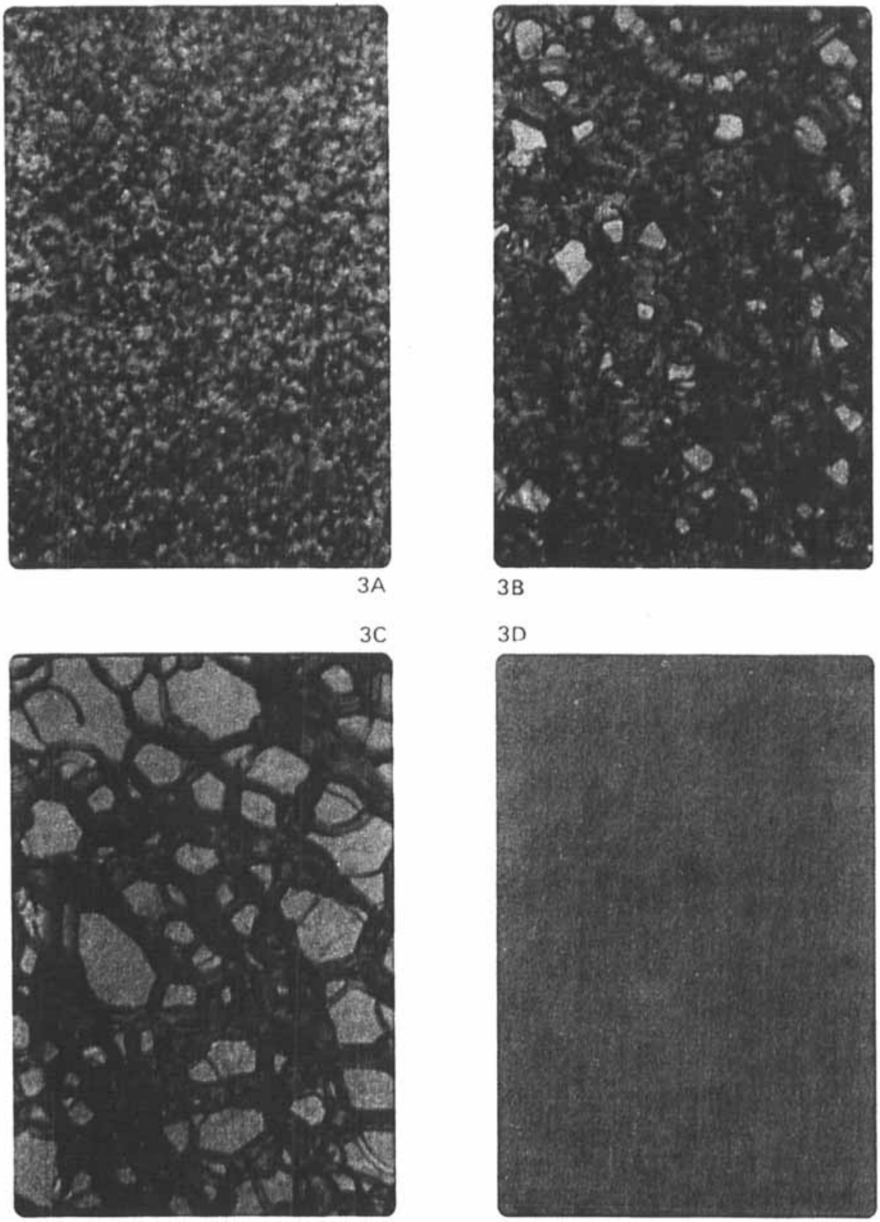
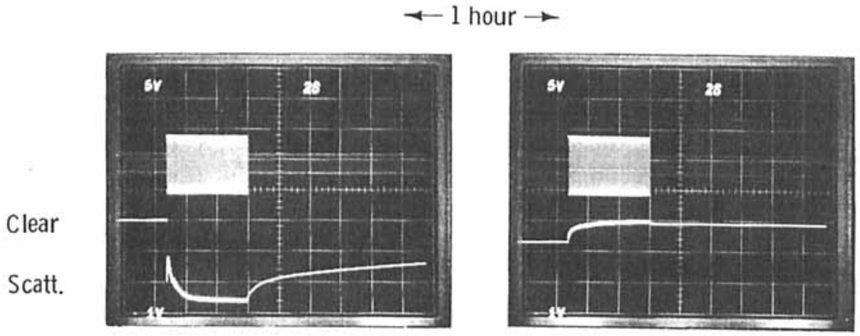
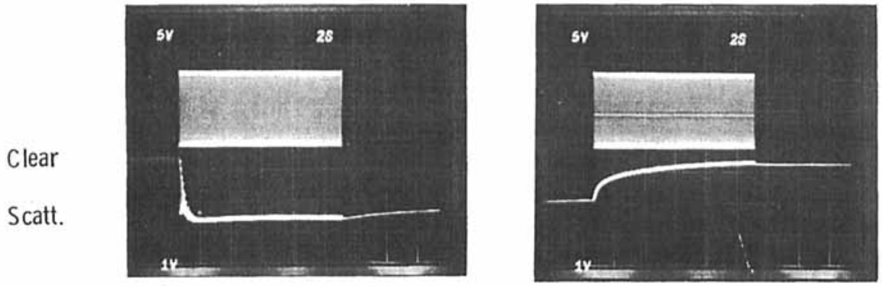


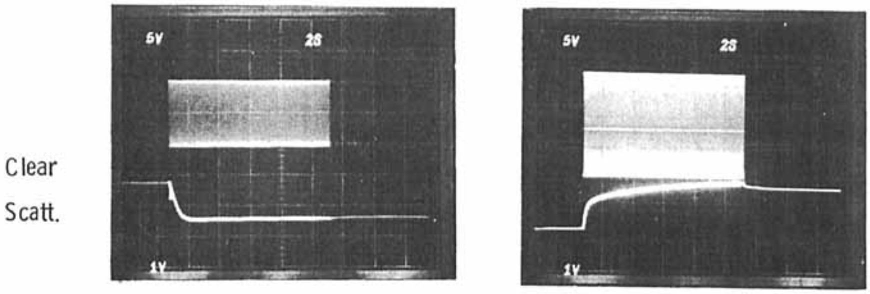
FIGURE 3 Sequence of photomicrographs showing the change in texture of the scattering state after the field has been turned off. Sample is a 10% solution of (-) 2-methylbutyl-p-(4-methoxy-benzylidene) amino cinnamate in m.b.b.a.
3a immediately after the field was turned off
3b approximately 1 minute later
3c approximately 5 minutes later
3d sample cleared with 30V 1 kHz sine wave.



10% chol. oleyl carb., 0.5% Hy 10, mbba
Turn on 100Hz sine Turn off 1000Hz sine



20% chol. oleyl carbonate in mbba
Turn on 10Hz sine Turn off 1000Hz



20% C. O. C., 0.5% Hy 10, mbba
Turn on 100Hz Turn off 1000Hz

FIGURE 4 Relative intensity for the clear and scattering state upper traces: applied field lower traces: diode outputs elapsed time between turn off and turn on: 1 hour
4a 10% cholesteryl oleyl carbonate, insufficient retention
4b 20% cholesteryl oleyl carbonate, scattering state last many weeks
4c as 4b but conductivity dopant added, low frequency response improves.

the solution behaves as a positive nematic under an electric field. The sample will be optically isotropic as long as the field is on but after the field is turned off realignment occurs which leaves the sample in a scattering state. This scattering state can be stable for a period of weeks but there is no electrical mechanism to turn the sample back to a permanently clear state.

This requirement on the sign of the anisotropy is the main difference between the solutions studied here and the cholesteryl chloride-myristate mixtures studied by Baessler *et al.*[11] or the positive anisotropic solutions studied by Heilmeier, Zanoni and Goldmacher.[12]

The liquid is brought into the scattering state by the turbulent flow resulting from negative dielectric but positive conductivity anisotropy. The sample is turned clear by choosing a frequency sufficiently high for carrier transport to be negligible, but of course well below the relaxation frequency.

It is clear from Figure 4 that adding charge carriers will make the system respond to higher frequency as is true for dynamic scattering. However the time needed to establish a stable scattering state (i.e., the gate period) does not decrease in the same proportion. The system only responds to a higher frequency signal. In this view the turn on frequency is a property of the liquid considered as an electrolytic solution rather than a property of individual dipole moments (Baessler, *et al.*, Meier, *et al.*). The effect of the dopant concentration on the turn on frequency can be obtained more quantitatively from the space charge relaxation time:

$$\tau = \frac{(\kappa^{-1})^2}{2D}.$$

The diffusion constant, D, is calculated from the mobility as

$$D = \mu\frac{kT}{c}$$

while κ is obtained from the usual expression

$$\kappa^2 = \frac{4\pi e^2 N}{\varepsilon kT\, 10^3}\sum c_i z_i^2.$$

Experimental values for μ are of the order of 10^{-6} cm^{2}V^{-1}sec^{-1} (see reference 8). c_i is the free ion concentration. For a conductivity of order 10^{-9} (ohm cm)$^{-1}$ c_i is typically 10^{-5} to 10^{-4} gmol/1. Inserting the remaining constants one obtains τ and thus the relaxation frequency (see Appendix). For this doping level the turn on frequency is between 1 and 10 kHz. For "undoped" samples having a conductivity of 10^{-11} (ohm cm)$^{-1}$ the turn on frequency is 10–100 Hz. This order of magnitude agrees well with the observations.

Finally, a note on the molecular interaction of the nematic solvent and the cholesteric solute. For positive cholesterics the interaction is clearly demonstrated optically, an electric field turns the sample optically isotropic and therefore all solvent molecules are misaligned as to the direction of the field. For negative cholesterics in m.b.b.a. the interaction can be judged from the molar polarization calculated from the data in Table II. Although the permittivity decreases with concentration, the molar polarization of the solute increases strongly with concentration. Thus the polarization of the solute is enhanced by that of the solvent. Data for the molar polarization of cholesteryl oleyl carbonate in neutral solvents are not available at this time making quantitative comparison impossible.

Acknowledgment

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Appendix

The ion sphere relaxation time is expressed as

$$\tau = \frac{(\kappa^{-1})^2}{2D} \qquad \kappa^{-1} \text{ in cm} \quad D \text{ in cm}^2\,\text{sec}^{-1}$$

which is in essence the Einstein-Smoluchowski relation. D is obtained from:

$$D = \mu \frac{kT}{e}$$

For $\mu \approx 10^{-6}$ cm^{2}V^{-1}sec^{-1} (see 6)

$$D = 2.6 \times 10^{-8}\ \text{cm}^2\text{sec}^{-1}$$

κ is obtained from

$$\kappa^2 = \frac{4\pi e^2 N}{\varepsilon k T\, 10^3} \sum c_i z_i^2$$

for a 1-1 electrolyte and $c_i = 10^{-4}$.

$$\kappa^2 = 0.17 \times 10^{13}$$

and thus $\tau \approx 10^{-5}$ for $c_i = 10^{-5}$, $\tau \approx 10^{-4}$, etc.