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# Cholesteric Structure-II Chemical Significance

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# Cholesteric Structure—II Chemical Significance

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## Introduction

The cholesteric phase represents a unique situation in nature in that a highly colored material does not absorb incident radiation but transmits and scatters light selectively. The colors are not dependent upon specific electronic arrangements in the molecules as in the more familiar dyes but, instead, are dependent on such factors as shape (steric factors) and dipole arrangement. Thus, materials which exhibit cholesteric phases may be affected by a difference in carbon chain length or by the position occupied by a functional group.

Normally when two different colored substances are mixed the absorption characteristics are additive in the mixture. However, when materials in the cholesteric phases are mixed, a single color peak results which represents the average effect of the molecules making up the system. This color is not related to the transmittance of the materials mixed. Therefore, Beer's Law does not apply. As a result, this average effect allows us to arrive at color effects in mixture which involve non-colored materials and without chemical reaction. The change in the optical properties of the liquid crystal may be quantitatively related to the components of a mixture.

These optical properties depend on a delicately balanced molecular arrangement. A change of shape or dipole moment or any other disturbance which interferes with the weak forces between molecules results in a dramatic change. Reflection, transmission, birefringence, circular dichroism, optical rotation, and color all undergo marked transformations.[1]

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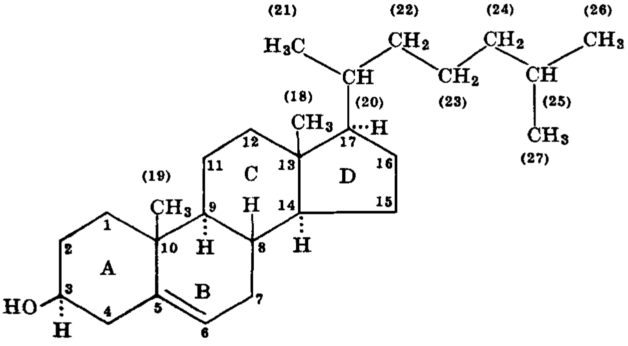
At our laboratories it was discovered that the adsorption or solution of gases, liquids, and solids in the cholesteric liquid crystal can affect its structure so that one or more of the optical properties are permanently or temporarily changed. By utilizing this general principle, an entirely new mode of material analysis is being developed.

## Cholesteric Structure Requirements

The cholesteric liquid state is primarily associated with the derivatives of sterols. Although cholesterol itself does not exhibit a liquid crystalline phase, an examination of its structure explains the formation of this phase in its derivatives.



(I)

If the angular methyl groups at $C_{10}$ and $C_{13}$ are visualized as projecting out of the plane of the paper, the side chain at $C_{17}$ and the hydroxyl group at $C_3$ will also project above the plane of the paper while the hydrogens which are dotted project below the plane of the paper. The result is a molecule which has a broad, flat configuration that may be visualized as zigzagging through the plane of the paper with one edge relatively smooth and one edge roughened by the side chain.

As one of the ways of determining the effect of molecular structure on the cholesteric phase, experiments were performed in

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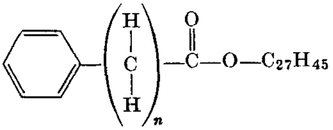
which the general planar configuration of the molecule was altered. This was done by saturating the double bond at $C_5$. If cholesterol is hydrogenated directly, the hydrogen at $C_5$ will project down and the general plane of the molecule will be preserved. This compound, which is called cholestanol, is also found associated in nature with cholesterol. The cholesterol-derived compound, coprostanol, which has the hydrogen at $C_5$ projecting out of the plane, is one of the elimination products of animals. In this case, the A ring is bent into the plane of the paper giving almost the effect of a hook.

All of the cholestanol compounds studied have a cholesteric phase which behaves optically in a similar manner as the phase formed by cholesterol derivatives. These include cholestanyl benzoate, cholestanyl nonanoate, cholestanyl acetate, and cholestanyl dihydrocinnamate. No coprostanol compounds have been found which exhibit a cholesteric phase. Thus, the dependence on a general planar configuration for the existence of the cholesteric liquid crystal phase is demonstrated.

The importance of the planar structure of the cholesteryl molecule in forming the cholesteric liquid crystal may be further confirmed by observing the cholesteryl esters of the omega-substituted phenyl-alkyl-monocarboxylic acids. These esters, which are listed in Table 1, have the following configuration.



(II)

These esters were prepared from the acid chlorides and cholesterol. The acids became increasingly difficult to obtain as the number of carbons in the alkyl side chain was increased. The materials, beginning with cholesteryl benzoate, that are separated from the cholesteryl ring by an even number of atoms all exhibited a strong cholesteric phase. By examining the configuration of cholesteryl benzoate, it was apparent that the benzene ring continues the planar configuration of the cholesteryl ring. This con-

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clusion became more evident upon examination of Taylor-Hirschfelder atomic models. The repetition of the results indicated that the alkyl chain is probably extended, for it if were randomly arranged, it should have made no difference whether the benzene ring was removed from the cholesteryl ring system by an odd or an even number of carbon atoms.

TABLE 1 Varying Chain Lengths and Cholesteric Phases of Cholesteryl Esters

| Cholesteryl ester | Carbon atoms in chain ($n$) | Melting point °C | Clearing point °C | Phases |
|---|---|---|---|---|
| Cholesteryl Benzoate | 0 | 146.6 | 180.6 | Cholesteric at melting point—Green at clearing point |
| Cholesteryl phenyl acetate | 1 | 118–119 | — | No cholesteric phase |
| Cholesteryl phenyl propionate | 2 | 109.4 | 111.7 | Cholesteric phase—Green at clearing point |
| Cholesteryl phenyl butyrate | 3 | 89.0–89.2 | — | No cholesteric phase |
| Cholesteryl phenyl valerate | 4 | 94.5–94.8 | 90.0 | Cholesteric phase—Blue at clearing point |

## Apparatus for Temperature *vs* Wavelength Measurement

In order to determine the temperature dependence of the cholesteric materials the device shown in Fig. 1 was used. If the cholesteric phase is illuminated by monochromatic light and the temperature varied so that the wavelength of maximum scattering passes through the wavelength of the source, the intensity of the light scattered will increase to a maximum and then decrease. If the source is a discharge lamp with a number of discreet emission lines these will be visible as peaks of intensity. The line which is being reflected is readily visible by observing the color of the cholesteric phase. The apparatus shown makes use of these principles by illuminating

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the phase with one of the lamps described in Table 2. The temperature of the aluminum block is varied by using a thermoelectric unit which is driven by a variable d.c. power supply. The block may be heated or cooled depending on the direction of current flow in the thermoelectric unit. The temperature range of this device as shown here is 120°C to −10° C. The temperature of the aluminum block is measured by a thermistor which drives the $X$ axis of an $X-Y$ recorder. As a cross reference and calibration source, a thermocouple is also used. Errors in this system occur in absolute measurements of temperature rather than temperature differences. The intensity of the light being scattered is measured by a photodetector and fed to the $Y$ axis of the recorder. The information which may be obtained in this manner is the temperature of each of the phase changes and the temperature of the scattering peaks.

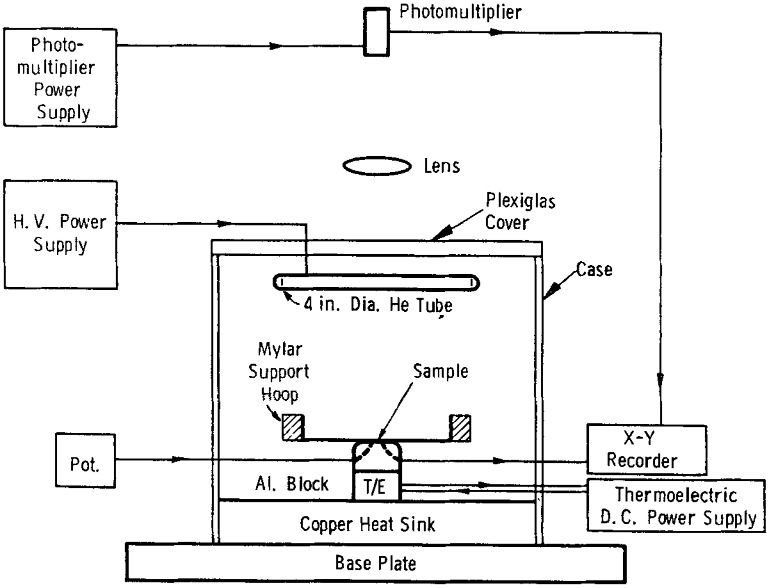

Figure 1. Apparatus used to determine temperature effects in cholesteric liquid.

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TABLE 2 Spectral Lamps for Wavelength *vs* Temperature Measurements

| Light source | Wavelength (Å) |
|---|---|
| Hg | |
| UV | 3663 |
| Purple | 4046 |
| Blue | 4358 |
| Green | 5460 |
| Yellow | 5780 |
| He | |
| UV | 3888 |
| Blue | 4685 |
| Green | 5015 |
| Yellow | 5875 |
| Red | 6560 |
| Cd | |
| Blue | 4799 |
| Green | 5085 |
| Red | 6438 |

The plane texture of the cholesteric phase is formed by casting a film from a suitable solvent, usually hexane or petroleum ether, onto a substrate film, the back of which has previously been

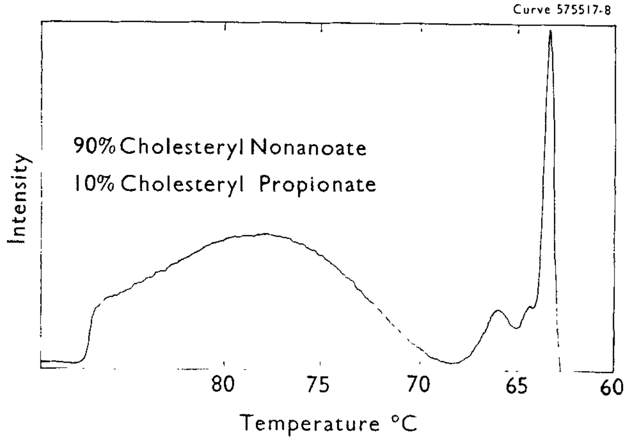

Figure 2. Typical output of the apparatus in Fig. 1 for He illumination.

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blackened. A 10% solution of most cholesterol derivatives has been found to give a film thickness of the 20 to 25 $\mu$ range when cast on 6 $\mu$ "Mylar"† film (25 gauge). The film is then placed on the block and the temperature is changed by varying the current through the thermoelectric device. In this manner a curve is recorded as shown in Fig. 2. This curve was made using a helium discharge for illumination. Each peak represents a maximum scattering position in terms of temperature. The temperature at which each peak occurs

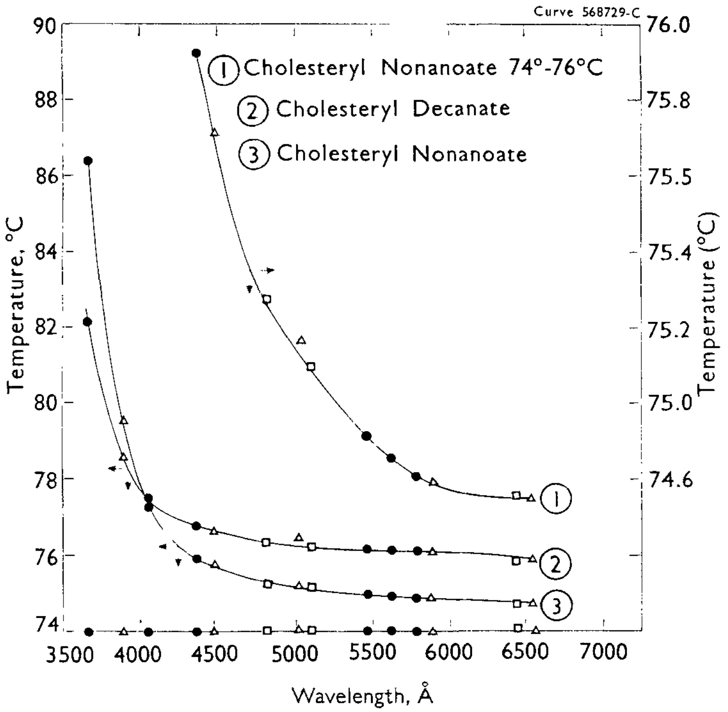

Figure 3. Wavelength of maximum scattering as a function of temperature for two pure materials.

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† Polyethylene Terephthalate—Product of E. I. DuPont de Nemours Co., Inc.

is then plotted against the wavelength of the particular line giving rise to the peak. All of the temperature *vs* wavelength functions presented here were derived in this fashion.

## Measurements of the Purity of Liquid Crystal Phases

One application of this device was the determination of purity and reproducibility of the temperature *vs* wavelength curve of the cholesteric liquid. In Fig. 3, the temperature *vs* wavelength curves of cholesteryl nonanoate and cholesteryl decanoate are shown. The temperature differences are measurable to 0.025°C with the present system. An expanded scale on the right is shown for cholesteryl nonanoate.

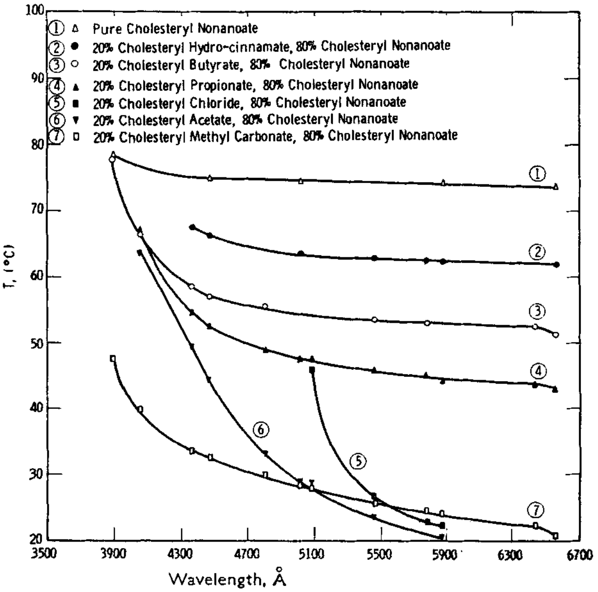

Figure 4. Wavelength of maximum scattering as a function of temperature for a number of mixtures of cholesteryl esters and cholesteryl nonanoate.

## Effects of Additions of Modifying Agents

Another use of this technique was to determine the effect of changes in molecular structure when known percentages of cholesterol derivatives and several oil-soluble materials were

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mixed with a standard cholesteric material. Cholesteryl nonanoate was used as a standard material and a number of cholesterol derivatives and fat soluble materials were added to it. One of the early projects was to add 20% of various cholesterol derivatives to

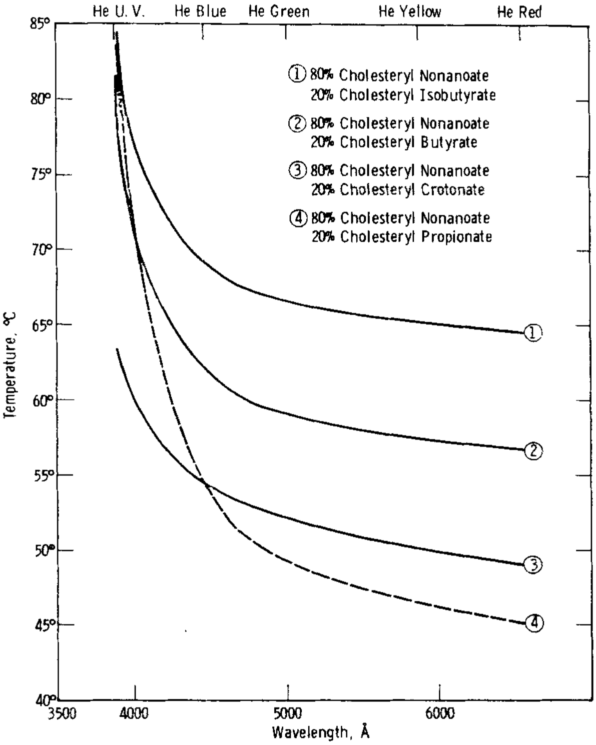

Figure 5. Wavelength of maximum scattering as a function of temperature for four closely related esters.

cholesteryl nonanoate. In Fig. 4, we see the effect of adding cholesterol esters of differing chain length. In this case, we can observe the shift in temperature sensitivity as a function of chain length. A change in chain length is readily identified by a change in the slope of the temperature *vs* wavelength curve. In Fig. 5, we see the results of adding isomeric derivatives of cholesterol which vary only in the position of carbon atoms; e.g., the case of cholesteryl butyrate

(III), cholesteryl isobutyrate (IV). In the case of cholesteryl butyrate and cholesteryl crotonate (V), the molecular structure differs only in the number of hydrogen atoms. In all cases a clear and distinct difference is seen in the behavior of the temperature *vs*

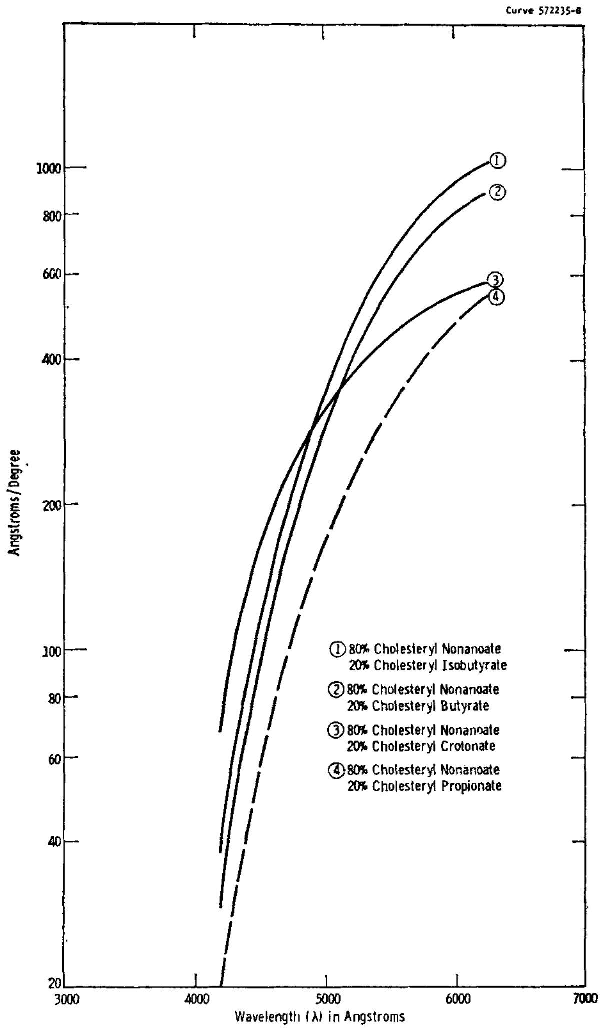

Figure. 6. Numerically determined slope of curves in Fig. 5.

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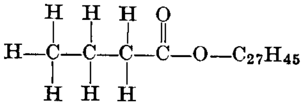
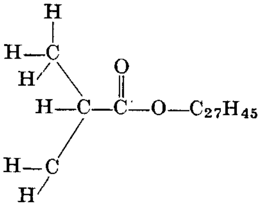
wavelength curves. Note that not only are the four curves displaced vertically with respect to each other, but at any wavelength they have significantly different slopes. This is illustrated by Fig. 6.

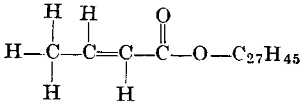


$H{-}CH_2{-}CH_2{-}CH_2{-}C(=O){-}O{-}C_{27}H_{45}$

(III)



(IV)



$H{-}CH_2{-}CH{=}CH{-}C(=O){-}O{-}C_{27}H_{45}$

(V)

In Fig. 7, we see the effect of the addition of various oil-soluble materials to a mixture of 80% cholesteryl nonanoate and 20% cholesteryl propionate. In this case, we do not see as distinct a change in the slope of the temperature *vs* wavelength curve as we do in the temperature displacement (Fig. 8).

From these data, it becomes clear that there are two distinct identifying features which might allow for the recognition of a change in structure in the cholesteric phase, and which would be recognizable as a change in color at a particular temperature. One is a change in slope of a temperature *vs* wavelength curve, and another is a translation of the temperature *vs* wavelength curve. In many cases we would expect that both of the above effects would be operative.

In Fig. 4, the material containing cholesteryl acetate shows less temperature effect than the material containing cholesteryl propionate. By finding the proper additive, the change of wavelength with temperature of a cholesteric liquid can be greatly decreased. An example of a stable additive which accomplished this purpose is cholesteryl chloride. In Fig. 9, the temperature *vs* wavelength curves are plotted for several different mixtures of cholesteryl chloride in cholesteryl nonanoate. In a large temperature interval (50° C), the 25% cholesteryl chloride is temperature insensitive.

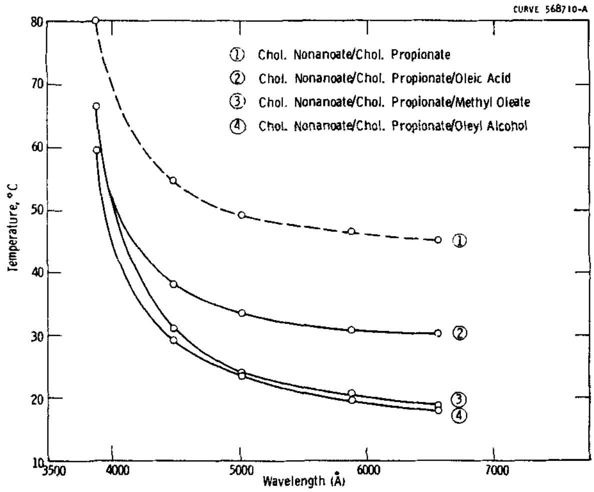


Figure 7. Wavelength of maximum scattering as a function of temperature for material containing 16 parts cholesteryl nonanoate, 4 parts cholesteryl propionate, and 1 part of three related oil soluble materials.

In this range a change in the per cent content of cholesteryl chloride is very easily seen as a change of color. Any materials which are similar to cholesteryl chloride in shape and size may be expected to behave in the same way. Examples of materials in this category are: cholesterol, cholesteryl bromide, and to a lesser degree, cholesteryl chloroformate.

Another manner of characterizing the mixtures of varying compositions of cholesteryl chloride in cholesteryl nonanoate is the effect of various solvents on the optical properties. Table 3[2] gives

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the reversible changes in color produced by various polar and non-polar organic solvents. The effect of polar solvents is a shift to the red, while the addition of a non-polar vapor shifts the color toward the blue. However, in some instances there is a tendency not to change the color at all (note the effect of trichloroethylene at 20%). It has been found that materials which have strong effects on the slope of the temperature *vs* wavelength curve tend to have a strong effect on this system, while additives whose main effect is to change the temperature at which the effect occurs, do not change the color greatly.

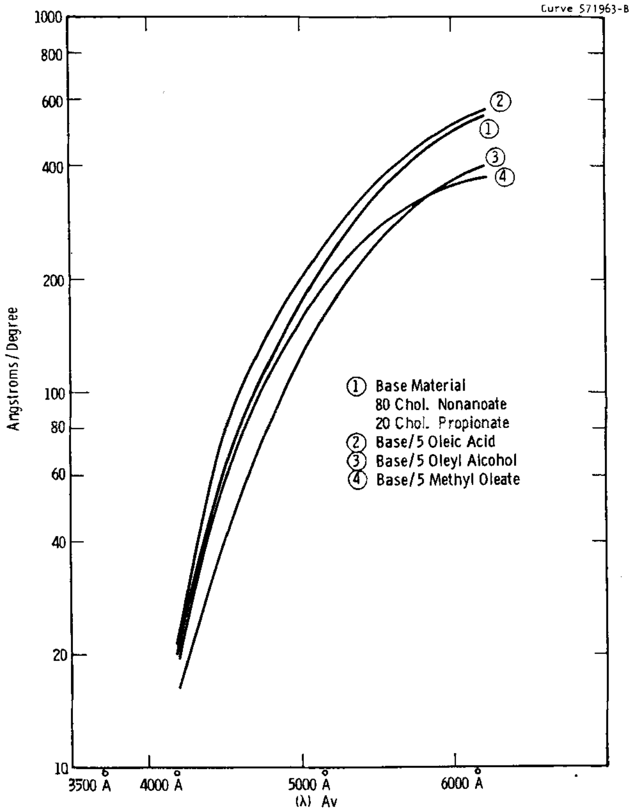

Figure 8. Slope of the curves in Fig. 7 numerically determined.

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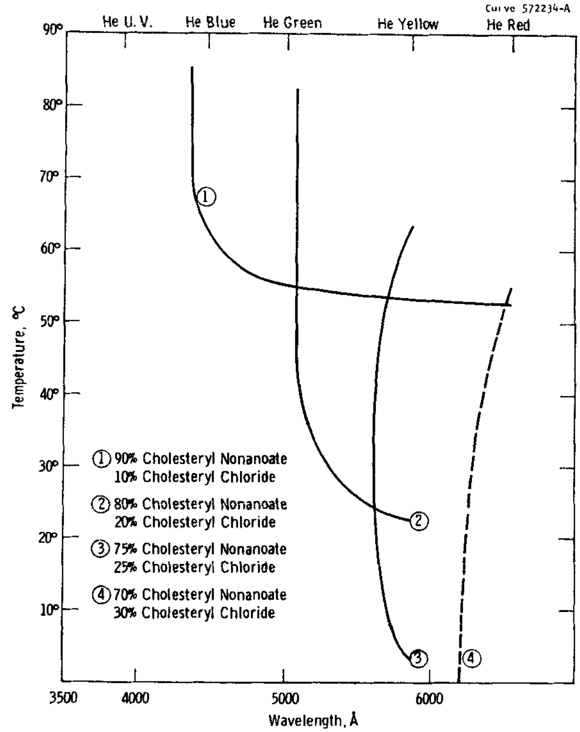

Figure 9. Wavelength of maximum scattering as a function of temperature for a number of mixtures of cholesteryl chloride and cholesteryl nonanoate.

TABLE 3 Response of Cholesteric Liquids to Solvent Vapors

| Cholesteric liquid composition | | | Benzene | Chloroform | Trichloro-ethylene | Methylene chloride | Petroleum ether |
|---|---|---|---|---|---|---|---|
| Cl | N | O | | | | | |
| 15 | 80 | 5 | Blue | Blue | Blue | Blue | Blue |
| 20 | 80 | | Blue | Red | No change | Red | Blue |
| 25 | 75 | | Red | Red | Red | Red | Blue |
| 30 | 70 | | Red | Red | Red | Red | Blue |

Cl = Cholesteryl chloride; N = Cholesteryl nonanoate; O = Cholesteryl oleate

The differences in temperature *vs* wavelength curves may be derived from two effects:

The temperature range of the cholesteric phase may be depressed with little change in the slope of the temperature *vs* wavelength curve. Almost any oil soluble additive to a cholesteric phase will give this effect.

The slope of the temperature *vs* wavelength curve may be changed. This effect is such that there may be a decrease or an increase in the slope in one wavelength region while the opposite occurs in another. This effect is closely related to the molecular structure of the additive and the materials making up the cholesteric phase.

## Conclusions

Cholesteric liquids have been shown to be sensitive to small changes in molecular structure and composition. The temperature dependence of the wavelength of maximum scattering yields information which may be used to determine materials integrity or composition. From these measurements both qualitative and quantitative interpretations may be made depending on the conditions of the measurement.

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