CHAPTER I

OPTICAL PROPERTIES OF A COMPENSATED CHOLESTERIC MIXTURE: NON-ABSORBING CASE

1. Introduction

The optical behaviour of mixtures of right-handed and left-handed cholesteric liquid crystals (compensated cholesteric mixtures) has been the subject matter of many investigations. Friedel (1922) showed that such a mixture results in a cholesteric structure whose pitch is sensitive to temperature and composition. For a given composition there is a temperature $T_N$ at which the optical rotation is zero and the structure becomes a nematic (infinite pitch); on either side of $T_N$ the rotations are of opposite signs indicating that the structure changes handedness on crossing this temperature. Recently, Sackmann et al. (1968) have directly determined the pitch as a function of temperature in a 1.75:1 weight mixture of cholesteryl chloride and cholestereryl myristate (CM) using laser diffraction techniques. They found that on increasing the temperature, the pitch of the sample gradually increased, becoming infinity at $42.5^\circ C$ and then decreased with further increase of temperature. Their results are shown in Figure 1. Adams et al. (1970)
**Figure 1**: Temperature dependence of the pitch of a 1.75:1 mixture of cholesteryl chloride and cholesteryl myristate. The experimental data are taken from Sackmann et al. 1968 (see Baessler et al. 1969).
measured the variation of pitch as a function of composition of a cholesteryl chloride-cholesteryl nonanoate system at room temperature using the dispersive reflection technique. Their experiments indicated that in a compensated mixture the pitch depends on the composition in a way similar to the dependence of pitch on temperature, i.e., the pitch of the sample increases with increase in concentration of cholesteryl chloride, attains an infinite value for a particular concentration and then decreases with additional increase of cholesteryl chloride. The optical rotatory power in a 1.75:1 by weight CM mixture was measured as a function of temperature by Baeesler et al. (1969), for two specimens of thickness 3 μm and 10 μm. Their results are presented in figure 2. It can be seen that at any particular temperature the optical rotatory power $\gamma$ is not the same for the two samples, the difference being far more marked around $T_N$. Teucher et al. (1971) have determined the rotatory dispersion for various temperatures in a 1.75:1 by weight CM mixture. Their studies show that the change in the sign of $\gamma$ at $T_N$ is due to the change in the helical sense of the system and that the system is right handed above $T_N$ and left handed below $T_N$. 
Figure 2: Rotatory power of a 1.75:1 mixture of cholesteryl chloride and cholesteryl myristate. (1) 10 μm sample, (2) 3 μm sample. (The dotted line indicates photomultiplier current at extinction position of polariser and analyser.) (Baessler et al. 1569).
The previous workers have discussed their results on the basis of the de Vries equation (de Vries 1951),

\[ \varphi = -\frac{2\pi}{P} \frac{a^2}{8 \lambda'^2 (1 - \lambda'^2)} \]  

(1a)

where \( P \) is the pitch of the helix, \( a = \frac{\varepsilon_1 - \varepsilon_2}{2\varepsilon} \), \( \varepsilon_1 \) and \( \varepsilon_2 \) are the principal dielectric constants of the untwisted structure, \( \varepsilon = \frac{1}{2}(\varepsilon_1 + \varepsilon_2) \), \( \lambda' = \frac{\lambda}{P\varepsilon} \), and \( \lambda \) is the wavelength in vacuum.

This equation predicts infinite optical rotation at \( T_N \) whereas experiments indicate aero rotation at \( T_N \). Furthermore, according to (1a), \( \varphi \) should be independent of sample thickness, whereas the results of Baessler et al. (1969) show that this is not the case.

In view of these discrepancies, detailed experimental studies of the optical rotatory power of a compensated mixture as a function of temperature/pitch for various sample thicknesses were undertaken. The results are presented in this chapter. It is shown that the de Vries equation is not valid at temperatures close to \( T_N \). The results are interpreted in terms of
a rigorous theory developed by Chandrasekhar et al. (1973), Kini (1977). A brief summary of this theory is also presented.

2. **Experiments**

The measurements were made on a mixture of cholesteryl chloride and cholesteryl myristate taken in the ratio of 1.6:1 by weight. (Cholesteryl chloride was prepared in the Laboratory and cholesteryl myristate was obtained from Vari-Light Corporation, USA).

The transition temperatures of the compounds used are given below.

**Cholesteryl chloride:**

\[
\text{Solid} \xrightarrow{95^\circ C} \text{isotropic} \xleftarrow{64^\circ C} \text{cholesteric}
\]

**Cholesteryl myristate:**

\[
\text{Solid} \xrightarrow{78^\circ C} \text{cholesteric} \xleftarrow{82^\circ C} \text{isotropic} \xleftarrow{75^\circ C} \text{smectic A}
\]
About 200–300 milligrams of the mixture was prepared in a small glass cup and it was heated in an oven to temperatures slightly above the cholesteric–isotropic transition temperature. It was stirred well with a glass rod to get homogeneous melt and then cooled to get the cholesteric phase.

The temperature of the sample was controlled by means of a specially constructed electric heater. It consisted of a copper tube of length 4.2 cm inner diameter 25 cm and outer diameter 5 cm. Around this tube, resistance wires were wound using mica sheets as insulator and the whole system was finally enclosed in a second copper tube. Glass windows were fixed on both sides of this outer tube to prevent air currents. Thermocouple wires contained in a ceramic capillary tube were introduced inside the heater through a small hole drilled in the copper tube. By controlling the current in the resistance wire it was possible to heat the system to any desired level. The temperature control was better than \( \pm 0.1^\circ C \).

A copper–constantan thermocouple was used to measure the sample temperature. Its thermo e.m.f., measured with a vernier potentiometer and a spot
deflection galvanometer system, was calibrated **against** a standard **thermometer** (Franz Küstner Nachf. KG., Dresden, G.D.R.). With this, the temperature could be measured to **an accuracy** of 0.05°C. The **optical rotation** was measured by **means** of a Winkel-Zeiss (Göttingen model No. 103071) polarimeter modified slightly to **accommodate** the complete heater assembly. The **polarimeter consists** of a Laurent's half shade and an **analysing nicol** mounted on a graduated disc. The **rotation** could be measured to **an accuracy** of 0.01°. The light **source** was a sodium lamp and all measurements were **carried out** at the wavelength 0.5893 pm.

Two identical glass discs (diameter 15 mm and thickness 2 mm) whose worked **surfaces** were flat to an order of $\sqrt[2]{L}$ were used to contain the sample. Measurements were made for three sample thicknesses, 12.7, 6.4 and 3 pm. **Samples** of 12.7 and 6.4 μm were obtained by using Dupont mylar **spacers** of thickness 0.5 and 0.25 mil respectively. [Here it was assumed that, **sample thickness** is equal to the nominal spacer thickness, though in practice the sample thickness is often slightly higher due to edge, effects.] The 3 μm sample was prepared without **using** any spacer and the thicknesses
was measured by forming interference fringes in the air spacer around the specimen. Since the plates could not be held perfectly parallel without a spacer, the thickness measurement of the 3 μm sample is estimated to be uncertain to ±25%.

The following procedure was adopted to get aligned samples: The substrates were thoroughly cleaned, successively with tsepol (wetting agent), concentrated NaOH, chromic acid, calcium carbonate and distilled water and then dried. The mixture heated to the cholesteric phase was sandwiched between the glass plates. Looking under a polarizing microscope one plate was displaced with respect to the other to and fro to get a well aligned plane textured sample. The entire cleaning process had to be repeated in cases where sample showed striations or domains. An aligned sample retained alignment more or less to the same extent at all temperatures in the cholesteric phase except in the vicinity of $T_N$. At temperatures in the neighbourhood of $T_N$ the sample developed inhomogeneities and at $T_N$ it usually consisted of small domains. The degree of misalignment at $T_N$ increased with increase in sample thickness. Also at $T_N$, it was not possible to completely cross the light
transmitted by the sample. This may be due to the depolarization of the incident light.

The optical rotation measurements were made on cooling from the isotropic phase. For reasons pointed out above the measurement of \( \varphi \) was comparatively difficult and less accurate very close to \( T_N \). This was particularly so in thick specimens where \( \varphi \) changes from a large positive value to a large negative value in a very small temperature interval around \( T_N \). Therefore unless the temperature is kept truly constant, measurements become practically impossible. It was possible to determine in the region between the positive and negative peaks for the 3 \( \mu m \) sample and to a lesser degree of accuracy for the 6.4 \( \mu m \) sample but not for the 12.7 \( \mu m \) sample. The experimental values of \( \varphi \) as a function of temperature (pitch) are given in figure 3. As the temperature is decreased, \( \varphi \) increases initially, reaches a maximum, then starts decreasing and falls to zero at \( T_N \). With further decrease of temperature \( \varphi \) changes sign, increases in magnitude, reaching a second maximum and from then on gradually decreases. The interesting result obtained was that both the positions and magnitudes of the peak values of \( \varphi \) are functions of the sample thickness.
Figure 3: Experimental rotatory power as a function of temperature for a 1.6 : 1 by weight mixture of cholesteryl chloride and choleesteryl myristate. Sample thickness (a) 3 ± 0.75 μm,
(b) 6.4 μm, (c) 12.7 μm.
The measurements show that the peak values increase in magnitude and move closer to $T_N$ with increase in sample thickness, and that $\phi$ is zero at $T_N$. This is very clear for the 3 $\mu$m and 6.4 $\mu$m samples but could not be established for the 12.7 $\mu$m sample due to experimental difficulties mentioned earlier.

The fact that $\phi$ is dependent on sample thickness, especially in the neighbourhood of $T_N$ and also that $\phi$ vanishes at $T_N$ establishes conclusively that equation (1a) is not valid, particularly close to $T_N$. We shall discuss the interpretation of these results on the basis of the rigorous theory.

3. **Theory**

Kirin (1977) has derived an exact expression for $\phi$ of a compensated mixture applying the Jones calculus (1941). This theory is reviewed here briefly.

The structure is regarded as a helically arranged pile of thin birefringent layers with the principal axes of the successive layers turned through a small angle $\beta$. The pitch $P$ is assumed to be greater than $\lambda$, the wavelength of light in vacuum so that the effect of reflections is neglected completely.
Let light be **incident normal** to the layers, i.e., along OZ. The principal axes of the first layer are assumed to be at an angle $\beta$ with respect to the coordinate axes OX, OY. The Jones retardation matrix with respect to the principal axes is written as

$$G = \begin{bmatrix}
e^{-i\gamma} & 0 \\
0 & e^{i\gamma}
\end{bmatrix}$$

where $\gamma = \frac{A}{\lambda} (\Delta \mu) \delta$ represents half the phase retardation produced by a single layer, $\Delta \mu = \mu_1 - \mu_2$ is the layer birefringence and $\delta$ is the layer thickness.

With respect to OX, OY this retardation matrix is

$$J_1 = S G S'$$

where

$$S = \begin{bmatrix}
\cos \beta & -\sin \beta \\
\sin \beta & \cos \beta
\end{bmatrix}$$

and $S' = S^{-1}$ is the transpose of $S$, so that $SS' = S' S = E$, the unit matrix.

The retardation matrix for 'n' layers is

$$J_n = S^n (GS')^n = \begin{bmatrix} a & b \\
c & d \end{bmatrix} , \quad (1b)$$
It can be shown that

\[(GS')^n = \frac{\sin n\theta}{\sin \theta} (GS') - \frac{\sin (n-1)\theta}{\sin \theta} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \]  \hspace{1cm} (2)

where \( \text{cob } \theta = \cos \beta \cos \gamma \).

since \( \beta \) and \( \gamma \) are small \( \{ \beta = \frac{2\pi}{P} b \). Taking \( b = 10 \times 10^{-3} \text{ cm} \) and \( P = 5 \times 10^{-4} \text{ cm}, \beta \sim 10^{-3} \]

\[ e^2 \sim \beta^2 + \gamma^2 \]  \hspace{1cm} (3)

Brom (1b) and (2)

\[ a = [\cos n\beta \cos n\theta + \frac{\tan \beta}{\tan \theta} \sin n\beta \sin n\theta] \]

\[ - i[\frac{\sin n\theta}{\sin \theta} \sin \gamma \cos (n+1)\beta] \]  \hspace{1cm} (4)

\[ b = [\frac{\tan \beta}{\tan \theta} \cos n\beta \sin n\theta - \sin n\beta \cos n\theta] \]

\[ - i[\frac{\sin n\theta}{\sin \theta} \sin \gamma \sin (n+1)\beta] \]  \hspace{1cm} (5a)

\[ c = -b^*, \hspace{0.5cm} d = a^*, \hspace{0.5cm} i = (-1)^{\frac{1}{2}} \]

where \( a^* \) and \( b^* \) are respectively the complex conjugates of \( a \) and \( b \).

A system of the above type can be treated as
a rotator and a retarder. If $\mathbf{J}_t$ is the total rotation produced by the system, $2\varphi$ the phase retardation and $\gamma$ the azimuth of the principal axes of the retarder,

$$\begin{vmatrix}
\cos \varphi & -\sin \varphi \\
\sin \varphi & \cos \varphi
\end{vmatrix}
\begin{vmatrix}
\cos \gamma & -\sin \gamma \\
\sin \gamma & \cos \gamma
\end{vmatrix}$$

$$\chi
\begin{vmatrix}
\exp(-i\varphi) & 0 \\
0 & \exp(i\varphi)
\end{vmatrix}
\begin{vmatrix}
\cos \gamma & \sin \gamma \\
-\sin \gamma & \cos \gamma
\end{vmatrix}$$

From (1b) and (5b)

$$a = \cos \varphi \cos \mathbf{J}_t - i \sin \varphi \cos(2\gamma + \mathbf{J}_t)$$

$$b = -\cos \varphi \sin \mathbf{J}_t - i \sin \varphi \sin(2\gamma + \mathbf{J}_t)$$

Equating real and imaginary parts of (4) and (6), and (5a) and (7), one gets

$$\mathbf{J}_t = n(\beta - \theta') \text{ radians}$$

$$\varphi = \cos^{-1} \left[ \frac{1 + \tan^2 \frac{n\theta'}{2}}{1 + \tan^2 \frac{n\theta}{2}} \right]$$

$$\gamma = \frac{1}{2}[(n + 1)\beta - \mathbf{J}_t]$$
where

\[ \theta' = \frac{1}{n} \tan^{-1} \left[ \frac{\tan \beta \tan n\theta}{\tan \theta} \right] \quad (10) \]

Equation (8) represents optical rotation for \( n \) layers, that is for a sample thickness \( np \).

The optical rotatory power is given by

\[ \phi = \frac{\theta' t}{np} = \frac{1}{p}(\beta - \theta') \text{ radians} \quad (11) \]

At temperatures well away from the nematic point \( T_N \), the pitch is relatively small, \( \beta \) becomes much larger than \( \gamma \), and from (3) and (10) \( \theta' \approx \theta \).

The optical rotatory power then becomes

\[ \phi \approx \frac{1}{p}(\beta - \theta) = \frac{1}{p}[\beta - (\beta^2 + \gamma^2)^{\frac{3}{2}}] \]

\[ = -\frac{1}{p} \frac{\gamma^2}{2\beta} \]

\[ = -\frac{\pi^2 (\Delta \mu)^2 p}{2\beta \lambda^2} \]

\[ = -\frac{\pi (\Delta \mu)^2 p}{4 \lambda^2} \quad (12) \]

which is the Mauguin-de Vries equation. As the
temperature approaches $T_N$ (i.e., for very high pitch values), $\varphi$ given by (11) departs from (1a) and (12).

At $T = T_N$, $P = \infty$, $\Theta' = \beta = 0$, and the rotation vanishes for all values of sample thickness, whereas (1a) and (12) predict infinite rotation.

Theoretical curves giving the dependence of the rotatory power on temperature of 1.75 : 1 CM mixture calculated using equation (11) are shown in Figure 4. The $\varphi$ values are calculated for $\lambda = 5893 \text{ Å}$ and layer thickness $b = 10 \text{ Å}$. The dependence of pitch on temperature has been taken from the data of Sackmann et al. (1968) for the 1.75:1 CM mixture. The layer birefringence $\Delta \mu$ at $20^\circ\text{C}$ and $55^\circ\text{C}$ were calculated by fitting the observed values (Baessler et al., 1969) of $\varphi$ in equation (12) at these, temperatures which are far away from $T_N$ and the intermediate values were obtained by interpolating linearly.

The curves in Figure 4 show that with increasing sample thickness, the positive and negative peaks in the rotatory power increase in height and also get closer to $T_N$ and thereby for thick samples the reversal in the sign of rotation takes place fairly abruptly. Comparing figures 3 with 4, it is clear that the trends in the observed data can be accounted for by this theory.
Figure 4: Theoretical variation of the rotatory power with temperature (and inverse pitch) for [1.75 : 1 CM (by weight) mixture] samples of thicknesses 2 μm, 6 μm and 10 μm. The broken curve is the rotatory power given by the Mauguin-de Vries equation.
$P^{-1}\text{ (micron}^{-1})$
References


Baessler, H., Laronge, T.M. and Labes, M.M. 1969


CHAPTER II

OPTICAL PROPERTIES OF A COMPENSATED CHOLESTERIC MIXTURE: ABSORBING CASE

1. Introduction

In the previous Chapter we presented some results on a non-absorbing compensated cholesteric mixture. In this Chapter we discuss the properties of an absorbing compensated mixture; in particular we investigate the circular dichroism of such a mixture. Saeva and Wysocki (1971) showed that the addition of a small quantity of linearly dichroic molecules in a non-absorbing cholesteric can give rise to circular dichroism in the region of the absorption band of the solute molecules. They dissolved a small quantity of \( n-(p\text{-methoxybenzyldiene})-p-n\text{-butylaniline} \) (MBBA) in a cholestereryl chloride–cholesteryl nonanoate system. Their circular dichroism spectra of the system for the cases of left-handed solvent and right-handed solvent as well as the absorption spectrum of MBBA are given in Figure 1. (In this thesis, we refer the circular dichroism due to solute molecules as 'induced circular dichroism' to distinguish
**Figure 1**

Circular dichroism (upper) and absorption spectrum (lower): \(-------\), \(6.3 \mu m\) film containing 52.9 mg of MBBA in 10.0 g, of 27.7:72.3 weight per cent cholesteryl chloride and cholesteryl nonanoate (right hand helix); \(-------\), \(11.7 \mu m\) film containing 63.19 mg of MBBA in 10.0 g, of 90.6:9.4 weight per cent cholesteryl chloride and cholesteryl nonanoate (left hand helix). The bands around \(550 \lambda (\mu m)\) are due to Bragg reflection and those around \(300 \lambda (\mu m)\) are due to the absorption by the solute molecules (Saeva and Wysocki 1971).
it from the circular dichroism that occurs at the reflection band in a cholesteric.) They demonstrated that changing the handedness of the solvent changes the sign of the induced circular dichroism (ICD) and that when the cholesteric medium is converted to a nematic (either by using a compensated mixture at temperature $T_N$ or by untwisting the cholesteric by the application of an electro field), the ICD reduces to zero indicating that a macroscopic helical structure is necessary for the induced effect and not just a chiral solvent.

Sackmann and Voss (1972), after studying ICD in several systems found that the sign of the ICD depends on the sign of the linear dichroism of the solute molecules. To interpret the origin of ICD in cholesterics, they assumed that the solute molecules adopt the same helical arrangement as the solvent molecules on a macroscopic scale. They also assumed that the solute molecules alone contribute to the absorption and linear dichroism of the cholesteric layers. Based on this model and the de Vries theory of light propagation in cholesterics, Sackmann and Voss theoretically calculated the ICD of cholesteric medium and showed that the predicted features are in
qualitative agreement with the observations.

However, in the above cases, the experimental observations pertain only to the regime \( \frac{\lambda_{\text{max}}}{\Delta \mu} \gg \frac{\Delta \mu}{2\mu} \)
i.e., \( P \ll \frac{\lambda_{\text{max}}}{\Delta \mu} \) (\( \lambda_{\text{max}} = P\mu \), \( \mu \) = average refractive index). The theoretical treatment of Sackmann and Voss holds good in this regime. In the present Chapter, studies are described on \( ICD \) as a function of temperature/pitch in the regime \( P \gg \frac{\lambda_{\text{max}}}{\Delta \mu} \) for different sample thicknesses. This has led to some interesting new observations that have so far been overlooked in previous studies.

2. Absorbing compensated cholesteric mixture

The sample was prepared by dissolving 1.48% by weight of \( \beta \)-carotene (Merck, Germany) in a 1.64:1 by weight cholesteryl chloride–cholesteryl myristate (CM) mixture. The dye \( \beta \)-carotene has a strong linear dichroic band around 0.48 μm. Figure 2 gives the polarised absorption spectra of \( \beta \)-carotene. The mixture taken in a small glass cup was heated in a even to a temperature slightly above the cholesteric–isotropic transition temperature and stirred well to get a homogeneous melt. As the melt was cooled it
Figure 2: Spectra of $5 \times 10^{-4}$ M β-carotene in a 1.9 : 1 by weight CM mixture ($T_N = 40^\circ C$). The sample was aligned for 12 hr. in a magnetic field of strength 20 KG applied along the helical axis ($T = 35^\circ C$). In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field. The oholeeteryl chloride and oholesteryl myristate molecules align perpendicular to the direction of the magnetic field (Sackmann 1968).
adopted a cholesteric structure.

To vary and to control the temperature of the sample an electrical heater (described in Chapter I) was used. The temperature of the sample was sensed by a copper–constantan thermocouple. The procedure for the calibration of the thermocouple and the measurement of thermo e.m.f. was similar to that explained in Chapter I.

A block diagram of the experimental set up to measure CD is given in figure 3. The light source was a tungsten filament lamp with a short focus lens positioned to give a parallel beam. It was run on a highly stabilized power supply. To improve the signal to noise ratio, a chopper, lock-in–amplifier system was used. The chopper was a metal wheel with apertures and rotated by a motor, the rotation of which was adjusted to chop the light beam at 321 cycles/second. A Mekee Pederson reflection grating monochromator (Model MP 108, USA) was used to get 0.5 μm radiation at which these experiments were conducted. Circularly polarised light was obtained by means of a Winkel–Zeiss polarising microscope attachment; it consisted of a nicol prism that could
Figure 3: A block diagram of the experimental arrangement used to determine the circular dichroism.

1 Tungsten filament light source
2 Mechanical chopper
3 Detector for reference signal
4 Monochromator
5 Circular polariser
6 Sample chamber
7 Photomultiplier tube
8 High tension power supply
9 Lock-in-amplifier
10 Oscilloscope
11 Microvoltmeter
12 Stabilised power supply.
be set at two orthogonal positions and a quarter wave plate with principal axes inclined at 45° with respect to the nicol. Depending on the position of the nicol the emergent light was either left circular or right circular. To avoid stray light the heater assembly was placed in a chamber provided with suitable windows for making these measurements. The light transmitted by the sample was detected by a photomultiplier (Model M10 PQS 29 Carl Zeiss, Zena). The signal was analysed by a lock-in-amplifier and the resulting signal was measured using a Philips D.C. microvoltmeter. (The lock-in-amplifier was constructed by Dr. S. R. Rajagopalan and Mr. A. Pujari of the Materials Science Division of National Aeronautical Laboratory, Bangalore and the measurements were carried out at their laboratory. I am grateful to them and to Dr. S. Ramaseshan, Head, Materials Science Division for extending the facilities and for helpful advice.)

The sample was sandwiched between two optically flat (∼λ/2) glass discs and the thickness of the sample was fixed using spacers. Measurements were made for five sample thicknesses 12.7, 9.5, 8, 6.3 and 4 μm. Standard Dupont sylar spacers of thickness 0.5 mil and 0.25 mil were used for the 12.7 and 64 μm film samples and mica spacers for 4, 8 and 9.5 μm samples. The uniformity in the thickness of the mica spacer was tested with a dial guage (Model MI/100 B Carl Zeiss,
Zena). The thickness measurements of mica spacers were accurate to ± µm. It was assumed that the sample thickness is equal to the spacer thickness. (It is known that the actual sample thickness may sometimes be slightly higher due to edge effects but no allowance was made for this in the present study.)

Plane texture films were obtained by cover plate displacement method described in Chapter 1. Before making the measurement of intensity, the alignment in the sample was checked using a polarizing microscope. An aligned sample retained alignment approximately to the same degree at all temperatures except in the vicinity of $T_N$ where it broke into small domains. The degree of misalignment at $T_N$ increased with increase in sample thickness. The determination of oirular dichroism in the cholesteric phase was started soon after cooling from the isotropic phase.

The transmitted intensities $I_R$ and $I_L$ were measured (as voltages in the DC microvoltmeter) for incident right- and left-circularly polarized light at every temperature and the circular dichroism was expressed as

$$D = \frac{I_R - I_L}{I_R + I_L + 2(I_R I_L)^{1/2}}$$
The **dichroic** power $\rho$ is given by

$$\rho = \frac{D}{t}$$

where $t = \text{sample thickness}$. (It will be noted that this definition of $D$ and $\rho$ eliminates the necessity for expressing the intensities in absolute units.)

Away from $T_N$ the error in the intensity measurements were less than 2%. But close to $T_N$ this error increased slightly. Also the error in the intensity measurement in the neighbourhood of $T_N$ increased with increasing sample thickness for reasons explained earlier.

3. **Results**

In figure 4 is given the experimental dependence of the **dichroic power** on temperature for various sample thicknesses. For any sample thickness the behaviour of $\rho$ versus temperature is analogous to that of the optical rotatory power in a non-absorbing compensated mixture (treated in Chapter I). At $T_N$ $\rho$ is equal to zero. It is negative on the lower temperature side and positive on the higher temperature
Figure 4: Experimental values of dichroic power versus temperature for different thicknesses of the sample in a 1.64 : 1 by weight mixture of cholesteryl chloride and ohololesteryl myristate containing 1.48% by weight of β-carotene.
side of $T_N$, the variation being almost symmetric about this temperature. $\beta$ increases rapidly as one moves away (on either side) from $T_N$ reaching a maximum at a characteristic temperature and then decreases gradually. The most interesting result from this figure is that the peak dichroic power decreases as the sample thickness increases in the range 4 to 12.7 $\mu$m. This behaviour is different from normal absorbing optically active materials thickness independent which exhibit circular dichroism. In addition, the position and the magnitudes of the peak values are functions of sample thickness, the peaks moving away from $T_N$ and becoming less and less sharp with increase in sample thickness. We shall now discuss the interpretation of these results on the basis of the rigorous theory due to Kini (1977).

4. Theory

Sackmann and Voss (1972) who established that ICD is due to helical stacking of linearly dichroic molecules have treated this problem in two extreme cases:

1) $\frac{\lambda}{\lambda_{\text{max}}}>\frac{\Delta \mu}{2\mu}$ i.e., $P \ll \frac{\lambda}{\Delta \mu}$
On this assumption they have obtained an expression for the circular dichroism which satisfactorily explains their experimental observations.

\[
\frac{\lambda}{\lambda_{\text{max}}} \ll \frac{\Delta \mu}{2\mu} \quad \text{i.e.,} \quad P \gg \frac{\lambda}{\Delta \mu}
\]

This holds good for very large pitch values, i.e., in systems like the twisted nematic devices (obtained by rotating the walls containing a nematic) where the normal waves are linear vibrations polarised along and perpendicular to the local director. In compensated mixtures, however, pitch values in the range \( P \gg \frac{\lambda}{\Delta \mu} \) also occur and at these pitch values the waves are elliptically polarised. Hence the treatment by Sackmann and Voss (1972) is not valid in this regime. The theory of optical rotatory power given in Chapter I has been extended by Kini (1977) to explain the optical properties of absorbing twisted structures.

As before the cholesteric structure is looked upon as a helical stack of very thin birefringent layers. Each layer is supposed to have uniaxial symmetry with the principal axis of the successive layers turned through a small angle \( \phi \). In addition
to the phase retardation \(2\gamma\) per layer, defined as
\[
2\gamma = \frac{2\pi(\Delta \mu)}{\lambda} \, \phi,
\]
one also has anisotropic absorption in the layers. The axes of the principal absorption coefficients \(k_1\) and \(k_2\) are assumed to coincide with the principal axes of the refractive indices \(\mu_1\) and \(\mu_2\). In this case, the Jones matrix of any layer with reference to its principal axes is

\[
\begin{bmatrix}
\exp(-i\gamma) & 0 \\
0 & \exp(i\gamma)
\end{bmatrix}
\begin{bmatrix}
\exp(-k_1 \phi) & 0 \\
0 & \exp(-k_2 \phi)
\end{bmatrix}
= \exp(-\alpha)
\begin{bmatrix}
\exp(-i\tilde{\gamma}) & 0 \\
0 & \exp(i\tilde{\gamma})
\end{bmatrix}
\]

(1)

where

\[
\alpha = \left(\frac{k_1 + k_2}{2}\right) \phi \quad \text{and} \quad \tilde{\gamma} = \gamma - \frac{k_1 - k_2}{2} \phi = \gamma - \delta.
\]

(Here the convention followed is that the phase factor at any point \(Z\) is given by \(\exp[-i(2\pi\mu Z/\lambda)]\)).

If the principal axes of the first layer be inclined at an angle \(\beta\) with respect to \(0X\), \(0Y\) of the
coordinate system $XYZ$ with light travelling along $OZ$, then the Jones matrix of the $n^{th}$ layer with respect to $XY$ is

$$G_n = S^n G_0 S^{-n}$$

(2)

where

$$S^n = \begin{bmatrix} \cos n\beta & -\sin n\beta \\ \sin n\beta & \cos n\beta \end{bmatrix}$$

and $S^n$ is the inverse of $S^{-n}$ (i.e., $S^n S^{-n} = E$, the unit matrix). For $n$ layers the net Jones matrix is given by

$$J_n = G_n \cdot G_{n-1} \cdot G_{n-2} \ldots \cdot G_2 \cdot G_1$$

$$= S^n G_0 S^{-n} S^{-n-1} G_0 S^{-n-2} \ldots S G_0 S^{-1}$$

But $S^m S^n = S^{m+n}$

Hence

$$J_n = S_n (G_0 S^{-1})^n$$

(3)

If $\lambda_1$ and $\lambda_2$ are the eigenvalues of $(G_0 S^{-1})$ then one can show that
\[(G_o S^{-1})^n = \frac{\lambda_1^n - \lambda^n}{\lambda_1 - \lambda_2} (G_o S^{-1}) - \lambda_1 \lambda_2 \frac{\lambda_1^{n-1} - \lambda_2^{n-1}}{\lambda_1 - \lambda_2} E\]

where \(\lambda_1\) and \(\lambda_2\) are given by

\[\lambda_1 = \exp(-\alpha)\exp(i\theta) \quad \text{and} \quad \lambda_2 = \exp(-\alpha)\exp(-i\theta)\]

with

\[\cos \hat{\theta} = \cos \gamma \cos \beta\]

Therefore

\[(G_o S^{-1})^n = \exp(-n\alpha) \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_o S^{-1}) - \exp[-(n+1)\alpha] \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} E\]

\[\approx \exp(-n\alpha) \left[ \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_o S^{-1}) - \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} E \right] \quad (4)\]

Since \(n\) is very large compared to unity.

Using (3) and (4) the net Jones matrix \(J_n\) can be worked in terms of \(\beta, \gamma, k_1, k_2\) and \(n\).

The matrix \(J_n\) can also be uniquely resolved into a rotator, a retarder, a circularly dichroic plate and a linearly dichroic plate. The unique matrix resolution is given by

\[J_n = \exp(-\gamma) \gamma^R \Sigma \Phi K \Sigma \gamma^{-1} \quad (5)\]
where

\[ \gamma = \begin{bmatrix} \cos \psi & -\sin \psi \\ \sin \psi & \cos \psi \end{bmatrix} \]

\[ R = \begin{bmatrix} \cos \frac{\sigma}{2} & -i \sinh \frac{\sigma}{2} \\ -i \sinh \frac{\sigma}{2} & \cosh \frac{\sigma}{2} \end{bmatrix} \]

\[ \Sigma = \begin{bmatrix} \cosh \frac{\sigma}{2} & i \sinh \frac{\sigma}{2} \\ -i \sinh \frac{\sigma}{2} & \cosh \frac{\sigma}{2} \end{bmatrix} \]

\[ \Phi = \begin{bmatrix} \exp(-i\psi) & 0 \\ 0 & \exp(i\psi) \end{bmatrix}, \quad \Lambda = \begin{bmatrix} \exp(-\Delta k/2) & 0 \\ 0 & \exp(\Delta k/2) \end{bmatrix} \]

where \( \varphi_t \) is the rotation, \( \sigma \) the imaginary part of rotation (equal in magnitude to \( 'D' \) at large values of \( \beta \)), \( 2\varphi \) the linear phase retardation, \( 4k \) the linear dichroism and \( \lambda \) the attenuation coefficient.

From (3), (4) and (5) it follows

\[ \varphi_t - i\sigma = n(\beta - \hat{\sigma}') \]

\[ \varphi - i\frac{\Delta k}{2} = \cos^{-1} \left( \frac{\sec^2 \frac{\hat{\sigma}'}{n^2}}{\sec^2 \frac{\hat{\sigma}}{n^2}} \right)^{\frac{1}{2}} \]

\[ \psi = \frac{1}{2}[(n + 1)\beta - \varphi_t] \quad (6) \]
\[ \chi = n\alpha \]

with

\[ \frac{\Delta \theta'}{\alpha} = \frac{1}{\alpha} \tan^{-1} \left( \frac{\tan \beta \tan \theta}{\tan \theta} \right) \]

There are two cases of special interest:

a) \( \beta \gg \gamma \)

In this case \( \varphi = \frac{\Delta k}{2} = 0 \)

and \( \delta_t = \delta - i\sigma \approx -\frac{\gamma^2}{2\beta} \)

Hence \( \delta_t = -\frac{n(\gamma^2 - \delta^2)}{2\beta} \)

\( \sigma = -\frac{n\gamma\delta}{\beta} \)

Therefore the linear dichroism of the layers not only results in circular dichroism but also makes a contribution to optical rotation which is opposite in sign to that due to linear birefringence. However this contribution is usually very small.

b) \( \beta \ll \gamma \)

In this case

\[ J_n \approx \exp(-n\alpha) \begin{bmatrix} \cos n\beta & -\sin n\beta \\ \sin n\beta & \cos n\beta \end{bmatrix} \begin{bmatrix} \exp(-i\gamma n) & 0 \\ 0 & \exp(i\gamma n) \end{bmatrix} \]
From this it follows that at any point in the medium there are two linear vibrations polarized along the local principal axes of the layer. As one moves along the axis in the direction of light propagation, the two vibrations rotate with the principal axes. The phase retardation and amplitude reduction undergone by these two vibrations are the same as in an untwisted nematic.

However at intermediate values of $\beta$ one has to use the complete expressions (6). The parameter $a$ which is the imaginary part of optical rotation is difficult to measure directly. It is for this reason that we have measured the parameter $D$ defined earlier. In fact far away from $T_N$, $|D| \approx |\sigma|$.

5. Discussion

To calculate $D$ theoretically one can use the following relation (which describe the nature of the emergent light when a right or left circularly polarized beam is incident on the specimen):

$$
\begin{pmatrix}
A_1 \\
A_2
\end{pmatrix} = \frac{1}{(2)^{1/2}} J_n \begin{pmatrix} 1 \\
1
\end{pmatrix} \text{ for right circular light.}
$$

$$
\begin{pmatrix}
B_1 \\
B_2
\end{pmatrix} = \frac{1}{(2)^{1/2}} J_n \begin{pmatrix} 1 \\
-1
\end{pmatrix} \text{ for left circular light.}
$$
Then
\[ I_R = |A_1|^2 + |A_2|^2 \]
\[ I_L = |B_1|^2 + |B_2|^2 \]

Figure 5 gives the variation of dichroic power with temperature (or inverse pitch) obtained theoretically for a typical system. The parameters \( P \) and \( \Delta \mu \) pertaining to CM mixture were the same as used in Chapter I. Further the layer birefringence and layer dichroism were assumed to decrease at the same rate with rise of temperature. The linear dichroism (\( \Delta k \)) was taken to be \( 0.1 \times 10^{-3} \) at \( \beta = 3 \times 10^{-3} \) on the lower temperature side of the nematic point. From the figure 5 one finds that \( \phi \) exhibits anomalous behaviour, the sign of the dichroism being opposite on either side of the nematic point. This prediction has been confirmed experimentally. The theory also leads to an interesting result regarding the dependence of the dielectric power \( \epsilon \) on sample thickness. In Table 1, the negative peak value of \( \phi \) for various sample thicknesses are given. It can be inferred that as the sample thickness is increased, \( \phi \) increases initially reaching a maximum and than decreases. For the range of sample thickness used in the experiments, calculated \( \phi \) does
Figure 5: Theoretical dependence of dichroic power on temperature and inverse pitch for a $1.75 : 1$ CM mixture of sample thickness 6 μm.
Table 1

<table>
<thead>
<tr>
<th>Sample thickness (in μm)</th>
<th>Negative peak value of θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>430.2</td>
</tr>
<tr>
<td>5</td>
<td>441.3</td>
</tr>
<tr>
<td>7</td>
<td>366.5</td>
</tr>
<tr>
<td>9</td>
<td>348.6</td>
</tr>
<tr>
<td>11</td>
<td>341.0</td>
</tr>
<tr>
<td>13</td>
<td>305.9</td>
</tr>
</tbody>
</table>
show broadly a decreasing trend with increasing sample thickness, though at a somewhat slower rate than observed experimentally. Considering the uncertainty in the assumed parameters, particularly $\Delta k$, it is gratifying that there is, at least, reasonably good qualitative agreement between theory and experiment.


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