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-methoxybenzylidene)-p-n-butyylaniline (MBBA) in a cholesteryl 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): \( \cdots \), 6.3 \( \mu \text{m} \) film containing 52.5 mg of MBBA in 10.0 g. of 27.7:72.3 weight per cent cholesteryl chloride and cholesteryl nonanoate (right hand helix); \( \cdots \), 11.7 \( \mu \text{m} \) 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\( \lambda \) (\( \mu \text{m} \)) are due to Bragg reflection and those around 300\( \lambda \) (\( \mu \text{m} \)) 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 electric 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 \( \frac{\lambda}{\lambda_{\text{max}}} \gg \frac{\Delta \mu}{2\mu} \)
i.e., \( P \ll \frac{\lambda}{\Delta \mu} (\lambda_{\text{max}} = P \mu, \mu = \text{average refractive index}) \). 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 \( P \gg \frac{\lambda}{\Delta \mu} \) 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 \( \mu \text{m} \). Figure 2 gives the polarised absorption spectra of \( \beta \)-carotene. The mixture taken in a small glass cup was heated in a oven 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 ($T_N = 40^\circ\text{C}$). The sample was aligned for 12 hr. in a magnetic field of strength 20 KG applied along the helical axis ($T = 35^\circ\text{C}$). In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field. The cholesteryl chloride and cholesteryl 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 polarizer
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 FQS 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 mylar spacers of thickness 0.5 mil and 0.25 mil were used for the 12.7 and 6.4 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 ±\(\frac{1}{2}\) 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 I. 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 circular 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

\[
D = \frac{I_R - I_L}{I_R + I_L + 2(I_R I_L)^{\frac{1}{2}}}
\]
The dichroic power $\phi$ is given by

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

where $t =$ sample thickness. (It will be noted that this definition of $D$ and $\phi$ 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 $\phi$ on temperature for various sample thicknesses. For any sample thickness the behaviour of $\phi$ versus temperature is analogous to that of the optical rotatory power in a non-absorbing compensated mixture (treated in Chapter I). At $T_N$, $\phi$ 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 cholesteryl myristate containing 1.48% by weight of β-carotene.
side of \( T_N \), the variation being almost symmetric about this temperature. \( \Delta \) 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 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) \[ \frac{\lambda}{\lambda_{\text{max}}} \gg \frac{\Delta \mu}{2\mu} \quad \text{i.e.,} \quad P \ll \frac{\lambda}{\Delta \mu} \]
On this assumption they have obtained an expression for the circular dichroism which satisfactorily explains their experimental observations.

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

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 \( \mathbf{P} \gg \frac{\lambda}{\Delta \mu} \) 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 \( \beta \). In addition
to the phase retardation $2\gamma$ per layer, defined as

$$2\gamma = \frac{2\pi}{\lambda}(\Delta \mu)\beta,$$

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

$$G = \begin{bmatrix}
\exp(-i\gamma) & 0 \\
0 & \exp(i\gamma)
\end{bmatrix} \begin{bmatrix}
\exp(-k_1\beta) & 0 \\
0 & \exp(-k_2\beta)
\end{bmatrix}$$

$$= \exp(-\alpha) \begin{bmatrix}
\exp(-i\hat{\gamma}) & 0 \\
0 & \exp(i\hat{\gamma})
\end{bmatrix}$$

(1)

where

$$\alpha = \frac{k_1 + k_2}{2}\beta \quad \text{and} \quad \hat{\gamma} = \gamma - i\frac{k_1 - k_2}{2}\beta = \gamma - i\delta.$$  

(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 $OX, OY$ 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

\[
J_n = G_n \cdot G_{n-1} \cdot G_{n-2} \cdots G_2 \cdot G_1 = S^n G_0 S^{-n} S^{n-1} G_0 S^{-(n-1)} \cdots SG_0 S^{-1}
\]

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
\[(G_0S^{-1})^n = \frac{\lambda_1^n - \lambda_2^n}{\lambda_1 - \lambda_2} (G_0S^{-1}) - \lambda_1\lambda_2 \frac{\lambda_1^{n-1} - \lambda_2^{n-1}}{\lambda_1 - \lambda_2} E\]

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

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

with

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

Therefore

\[(G_0S^{-1})^n = \exp(-n\alpha) \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_0S^{-1}) - \exp[-(n+1)\alpha] \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} \sin \theta\]

\[\approx \exp(-n\alpha) \left[ \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_0S^{-1}) - \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} E \right] \tag{4}\]

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

\[J_n = \exp(-\chi)\gamma R \sum \delta K \sum \gamma^{-l} \tag{5}\]
where

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

\[ \hat{R} = \begin{bmatrix} \cos \phi_t & -\sin \phi_t \\ \sin \phi_t & \cos \phi_t \end{bmatrix} \]

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

\[ \hat{\Phi} = \begin{bmatrix} \exp(-i\phi) & 0 \\ 0 & \exp(i\phi) \end{bmatrix} \]

\[ K = \begin{bmatrix} \exp(-i\Delta k/2) & 0 \\ 0 & \exp(i\Delta k/2) \end{bmatrix} \]

where \( \phi_t \) is the rotation, \( \sigma \) the imaginary part of rotation (equal in magnitude to \( \Delta \) at large values of \( \beta \)), \( 2\phi \) the linear phase retardation, \( \Delta k \) the linear dichroism and \( \chi \) the attenuation coefficient.

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

\[ \phi_t - i\sigma = n(\beta - \theta') \]

\[ \phi - i\Delta k/2 = \cos^{-1} \left[ \frac{\sec^2 \frac{n\theta}{2}}{\sec^2 \frac{n\theta'}{2}} \right] \]

\[ \psi = \frac{1}{2} \left[ (n + 1)\beta - \phi_t \right] \]

(6)
\[ \chi = n\alpha \]

with
\[ \hat{\theta'} = \frac{1}{n} \tan^{-1} \left[ \frac{\tan \beta \tan n\theta}{\tan \hat{\theta}} \right] \]

There are two cases of special interest:

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

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

and
\[ \hat{\beta}_t = \hat{\beta}_t - i\sigma \approx -\frac{\gamma^2}{2\delta} \]

Hence
\[ \hat{\beta}_t = -\frac{n(\gamma^2 - \delta^2)}{2\delta} \]

\[ \sigma = -\frac{n\gamma\delta}{\beta} \]

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 $\sigma$ 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 relations (which describe the nature of the emergent light when a right or left circularly polarized beam is incident on the specimen):

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \frac{1}{(2)\pi} J_n \begin{bmatrix} 1 \\ i \end{bmatrix}$$ for right circular light.

$$\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = \frac{1}{(2)\pi} J_n \begin{bmatrix} 1 \\ -i \end{bmatrix}$$ for left circular light.
Then

\[ I_R = \left| A_1 \right|^2 + \left| A_2 \right|^2 \]

\[ I_L = \left| B_1 \right|^2 + \left| B_2 \right|^2 \]

Figure 5 gives the variation of dichroic power \( P \) 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 \( P \) 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 dichroic power \( P \) on sample thickness. In table 1, the negative peak value of \( P \) for various sample thicknesses are given. It can be inferred that as the sample thickness is increased, \( P \) increases initially reaching a maximum and then decreases. For the range of sample thickness used in the experiments, calculated \( P \) does
Dichroic power $\phi$ (cm$^{-1}$)
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>
<thead>
<tr>
<th>Sample thickness (in μm)</th>
<th>Negative peak value of $h$</th>
</tr>
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<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>
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<td>13</td>
<td>305.9</td>
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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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