CHAPTER-7

PHASE TRANSITION STUDY OF CHOLESTERYL OLEATE LIQUID CRYSTAL AND ESTIMATION OF DIPOLE MOMENT

7.1 INTRODUCTION

Liquid crystals thus represent a new state of matter quite distinct from solid or liquid phase. Friedel in 1922 suggested a new name “mesophase” to these intermediate phases. An essential requirement for the mesomorphism to occur is that the molecules must be highly geometrically anisotropic. Depending upon the detailed molecular geometry, the system may pass through one or more mesophases before it is transformed from solid to isotropic and vice-versa. Transition to these states may be brought about by thermal process (thermotropic liquid crystals). When the mesophases are obtained only in one direction at thermal cycle, the thermotropic liquid crystals are called monotropic. Thermotropic liquid crystals are broadly classified as nematic, cholesteric and smectic. The nematic liquid crystals have a high degree of long range orientational order of molecules, but no long range translational order. The molecules of the nematics are spontaneously oriented with their long axis approximately parallel to a direction represented by a unit vector \( \hat{n} \) and called the director. The preferred direction usually varies from point to point in the medium, but a homogeneously aligned specimen is optically uniaxial, positive and strongly birefringent. Therefore in nematics the complete rotational symmetry is preserved. Along with the long range orientational order this mesophase retains the character of fluidity. Due to it the molecules can slide past one another retaining their parallelism. The degree of orientation of the nematic molecules with respect to the director has been defined by the parameter “S” the order parameter. It was first introduced by Tsvetkov as
\[ S = \frac{1}{2} < 3 \cos^2 \theta - 1 > \]  

(1)

\('\theta'\) is the angle which the long molecular axis makes with \( \hat{n} \). For normal liquids with random orientation \( S=0 \) and for perfectly parallel alignment \( S=1 \). In the nematics \( S \) has the values from \( S=0.4 \) to \( 0.7 \) and is strongly temperature dependent. The order parameter has been related to many experimentally determinable quantities\(^5^\text{--}^\text{13} \). Reviews on this subject are available\(^\text{14}^\text{--}^\text{15} \).

The cholesteric mesophases are composed of optically active molecules. The center of gravity have no long range order i.e. the molecules can slide past one another. The molecular orientation shows a preferred axis labelled by \( \hat{n} \) likes nematics. However the direction of \( \hat{n} \) is not held constant in space and therefore the molecules in cholesteryl are arranged into layers with long range directional order in the plane of the layer. The characteristic of different liquid crystal reviewed by Blinovs\(^1\text{6} \) and Sackmann\(^1\text{7} \) et al.

In this work we have chosen cholesteryl oleate for the study of phase transition using data of refractive index measured by Abbe's refractometer. The variation of molar polarizability \( M_r \) and distorted polarizability (electronic + atomic) as well as orientational polarizability are studied as a function of temperature using the data of static permittivity and permittivity at high frequency as well as the density. We have computed dipole moment. A qualitative information has been given about molecular interaction using significant liquid structure theory used in the earlier chapter-5.

7.2 THEORETICAL DETAILS

We know that the total polarizability is given by

\[ \alpha_T = \alpha_e + \alpha_s + \alpha_o \]  

(2)

where \( \alpha_e \rightarrow \) electrical polarizability
\[ \alpha_s \rightarrow \text{atomic polarizability} \]

\[ \alpha_o \rightarrow \text{orientational polarizability} \]

From Debye\textsuperscript{21} eq. we know

\[
\frac{\varepsilon_s - 1}{\varepsilon_s + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \alpha_o + \frac{4\pi N}{3} \alpha_s + \frac{4\pi N}{3} \frac{\mu_o^2}{3kT} \tag{3}
\]

Also

\[
\frac{\varepsilon_o - 1}{\varepsilon_o + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \alpha_o + \frac{4\pi N}{3} \alpha_s \tag{4}
\]

Subtracting eq. (3) from eq. (2) we get

\[
\left[ \frac{\varepsilon_s - 1}{\varepsilon_s + 2} - \frac{\varepsilon_o - 1}{\varepsilon_o + 2} \right] \frac{M}{\rho} = \frac{4\pi N}{9} \frac{\mu_o^2}{kT} \tag{5}
\]

\[ Y = m \left( \frac{1}{T} \right) \tag{6} \]

where

\[ Y = \left[ \left( \frac{\varepsilon_s - 1}{\varepsilon_s + 2} \right) - \left( \frac{\varepsilon_o - 1}{\varepsilon_o + 2} \right) \right] \frac{M}{\rho} \tag{7} \]

and slope

\[ m = \frac{4\pi N}{9} \frac{\mu^2}{k} \tag{8} \]

if we put

\[ X = \frac{1}{T} \tag{9} \]

we get

\[ Y = mX \tag{10} \]

By using least square fit method we can compute the slope and the intercept.

The slope gives us the value of the dipole moment i.e.

\[ \mu = k \sqrt{\text{(Slope)}} \tag{11} \]
where
\[ k_1 = \frac{3}{2} \sqrt{\frac{k}{\pi N}} \]  

Blinov et al\textsuperscript{16} have given an approximate relation for the dipole moment which involves the transition temperature for the nematic phase making an approximation for distribution parameter value, the dipole moment have been calculated which involves the experimental data of density and transition temperature. The expression given gives a minimum value of the dipole moment. It has been expressed\textsuperscript{16} as

\[ \mu \geq \sqrt{\frac{9 k T M}{4 \pi \rho N_A}} \]  

\[ = k_2 \sqrt{\frac{T M}{\rho}} \]  

where
\[ k_2 = \frac{3}{2} \sqrt{\frac{k}{\pi N_A}} \]  

where \( M \) is the molecular weight and \( \rho \) is the density. This eq. has been used for determination of dipole moment of para azoxy anisole (PAA). If we put \( M=200 \) (For PAA), \( \rho=1 \text{ gm/cm}^3 \) and transition temperature \( T=400^\circ \text{C} \) as typical values the dipole moment comes around 3.6D which is greater than the value of dipole moment for PAA i.e. 2.5 D.

The expression derived here above in eq.(11) although emperical but it is based on the dielectric data and it seems to be better form for computing dipole moment than given by Blinov et al\textsuperscript{16} in eq.(13).

Usually the atomic polarizability in almost all the cases does not exceed 10% of the total polarizability. Ignoring the term \( \alpha_a \) in the distorted expression of the polarizability we get molar refraction as a function of electronic polarizability which could be estimated by making measurement of the refractive index under the assumption \( \varepsilon_{\infty} = n_d^2 \) the molar
refraction is given by

\[ M_R = \left( \frac{n_d^2 - 1}{n_d^2 + 2} \right) \frac{M}{\rho} = \frac{4}{3} \pi \alpha_e N \]  

(16)

We intend to plot molar refraction as a function of temperature and determine the value of volume much below the freezing point i.e. the limit of 0°C. We assume that this molar refraction will give us a volume \( V_s \) for solid contribution.

We can compute solid like volume \( V_s \). From the significant liquid structure theory any properly could be expressed

\[ X = (V_s / V) X_s + [(V - V_s) / V] X_g \]  

(17)

Also

\[ V = V_m + V_{dd} + V_{sp} \]  

(18)

where \( V_m \) = contribution of electronic polarizability

\( V_{dd} \) = contribution of dipole-dipole interaction

\( V_{sp} \) = contribution of London dispersion attractive forces and exchange repulsive forces
## TABLE - 1

Experimental parameter for cholesteryl Oleate (Molecular weight 651.12).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temp. °C</th>
<th>ρ (gm/cc)</th>
<th>$\varepsilon_s - 1$</th>
<th>$\frac{V = M/\rho}{\varepsilon_s + 2}$ (cc)</th>
<th>n_d</th>
<th>$\frac{n_d^2 - 1}{n_d^2 + 2}$</th>
<th>Y</th>
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<tr>
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<td>53</td>
<td>0.9320</td>
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<td>1.493</td>
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<tr>
<td>3</td>
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<td>0.380</td>
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<td>0.2901</td>
<td>63.02</td>
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<tr>
<td>4</td>
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<td>700.88</td>
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<tr>
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<td>0.9243</td>
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<td>704.44</td>
<td>1.488</td>
<td>0.288</td>
<td>61.03</td>
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<td>7</td>
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<td>0.375</td>
<td>706.35</td>
<td>1.487</td>
<td>0.287</td>
<td>61.72</td>
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### TABLE - 2

Estimation of dipole moment.

<table>
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<tr>
<th>Sr. No.</th>
<th>1/T (°K)</th>
<th>Y</th>
<th>V = M/ρ (cc)</th>
<th>μ&lt;sub&gt;s&lt;/sub&gt; (D)</th>
<th>present work μ(D)</th>
</tr>
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<td>706.35</td>
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</table>

Using Slope(m) = 23398

\[ \mu = 1.96 \times 10^{-18} \text{ cgs unit} = 1.96 \text{ D} \]
TABLE - 3

Qualitative estimation of contribution intermolecular forces assuming $V_s=657.70$ cm$^3$ at 0°C.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temp $^\circ$K</th>
<th>$\frac{V_s}{V} \times 100%$</th>
<th>$\frac{V-V_s}{V} \times 100%$</th>
<th>$\frac{M_R}{V} \times 100%$</th>
</tr>
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<tr>
<td>1</td>
<td>326</td>
<td>94.1</td>
<td>5.9</td>
<td>29.1</td>
</tr>
<tr>
<td>2</td>
<td>327</td>
<td>94.1</td>
<td>5.9</td>
<td>29.1</td>
</tr>
<tr>
<td>3</td>
<td>328</td>
<td>94.0</td>
<td>6.0</td>
<td>29.0</td>
</tr>
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<td>4</td>
<td>331</td>
<td>94.0</td>
<td>6.2</td>
<td>29.0</td>
</tr>
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</tr>
<tr>
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<td>28.8</td>
</tr>
<tr>
<td>7</td>
<td>343</td>
<td>93.1</td>
<td>6.9</td>
<td>28.8</td>
</tr>
</tbody>
</table>
Figure 1. Variation of molar refraction as a function of Temperature.
\[ \text{C}_{45}\text{H}_{78}\text{O}_{2} \]
Mol. wt. = 651.12

(STRUCTURE FORMULA OF CHOLESTERYL OLEATE)
7.3 RESULTS AND DISCUSSION

The variation of molar refraction with temperature is given in Fig. (1). The approximate region of $K \rightarrow Ch$, $Ch \rightarrow I$ have been indicated in this diagram. The expression parameters$^{19}$ are given in Table-1. Table-2 gives an estimate of the dipole moment using an approximate formula$^{16}$ using the literature given in eq.(13). We have used the least square fit method between molar refraction ($M_r$) and temperature to obtain the value of slope for the calculation of dipole moment in the present work using eq.(11). The variation of orientational polarization with temperature is given in Table-2. The formula derived and method of calculation of dipole moment given in this work gives the reasonable value for the dipole moment and it is better than the formula given by Blinov$^{16}$ in eq.(13).

An examination of the Table-2 shows that there is slight change in the value of dipole moment in increasing order with the increase of the temperature assuming that the dipole moment may be independent of the temperature. The average value along with the mean deviation comes about $6.19 \pm 0.06$. This value may correspond to value at transition temperature $327.9^oK$ as per relation given by Blinov$^{16}$.

This value is much more than eq.(13). Our value (1.96 D) computed using eq.(11). The value 1.96 D obtained in this work is close agreement with the values 1.92 D for isotropic phase and 2.73 D for cholesteriac phase.

We have assumed the volume of the solid like structure of cholesterate oleate at about $0^oC$ to be $65.770 \text{ cm}^3$. Table-3 gives the contribution of intermolecular forces using significant liquid structure theory.
REFERENCES


