CHAPTER 3
EXPRIMENTAL STUDIES

3.1 INTRODUCTION

This chapter gives a brief account of the various experimental techniques used to determination of refractive index, density and birefringence of various compounds in the liquid crystalline phase. Also the description of the polarizing microscope to study the textures of different liquid crystalline materials, temperature controller, Goniometer spectrometer, construction of hollow glass prism and Abbe refractometer are discussed.

3.2 THE POLARIZING MICROSCOPE

The polarizing microscope is used to examine liquid crystalline samples between crossed polarizers and is shown in Figure 3.1. The Leitz-Orthoplan microscope is one of the important variant equipment for the observations of the optical textures.

The specimen is taken in the form of thin film between a slide (7.5x2.5cm²) and cover slip with the sample thickness varying between 30 μ to 50 μ. The specimen is melted in between the cover slip and glass slide and sealed with araldite or epoxy cement. The prepared slide is kept on a specially constructed hot stage with a temperature controller unit for observations under the polarizing microscope.

Electrical field effect measurements were carried out by the usual experimental setup [1], which consists of tin oxide coated transparent conducting glass plates (6.0 x 2.5 cm²) and the sample is sandwiched between these two glass plates. Teflon spacers having thickness of d=39μm were used and an electrical field were applied by AC or DC sources through the conducting plates.
Observations were made using a polarizing microscope in conjunction with a hot stage.

3.2.1 LIQUID CRYSTALS UNDER MICROSCOPE

The anisotropy of mesogenic molecules, along with the degree of orientational order in the liquid crystal phases, leads to several interesting optical phenomena. Light passing through a liquid crystal sample will experience different refractive indices depending on the polarization direction relative to the local director orientation. This means that the component polarized parallel to the director will traverse the medium with a different speed from that of the perpendicularly polarized component. This affects the phase relation between the components and leads to a change in polarization state. For an instance, if the incident beam is linearly polarized the polarization direction is generally changed on passage through the sample and the light may become elliptically polarized. When we were looking at the liquid crystals in a microscope, the sample is inserted between the crossed polarizers. At first the incident light is linearly polarized in one specific direction, since the polarizers are crossed no light would emerge through the second polarizer if the liquid crystal were absent. But when the light passes through the anisotropic sample its polarization state is altered and thus the some of it may pass through the second polarizer (often referred to as the analyzer). The sample now often appears in bright colours, since the effect is wavelength dependent. The good contrasts textures, which were observed, can be photographed.

3.3 EXPERIMENTAL DETERMINATION OF THE REFRACTIVE INDEX OF THE LIQUID CRYSTAL

The refractive indices were determined using Abbe refractometer and also a hollow glass prism in conjunction with a precession Goniometer spectrometer.
3.3.1 ABBE REFRACTOMETER

Abbe refractometer is shown in Figure 3.2, consists of two prisms between which the sample whose the refractive indices have to be determined is introduced. The combination of prisms containing liquid crystalline material, which is illuminated by a monochromatic sodium light (\(\lambda=5893\text{Å}\)). The refractometer is in conjunction with a temperature bath from which hot water can be circulated to maintain the sample at different temperatures. Initially the refractometer is standardized using distilled water at room temperature. Before introducing the liquid crystalline material between the prisms, their surfaces must be thoroughly rubbed using cotton in one direction to achieve homogeneous alignment of the sample. In the field of view two lines of demarcation of slightly different polarization are observed. The horizontal polarization corresponds to the ordinary ray and vertical polarization is due to the extraordinary ray. By matching the cross wire, the refractive indices of the ordinary ray and extraordinary ray can be read directly. Because of hot water circulation, it is not possible to determine the refractive indices of materials beyond 80 °C.

We have measured the refractive indices of mixtures having lower isotropic transition temperatures using Abbe refractometer and compared the results with an independent measurement using Goniometer spectrometer.

3.3.2 GONIOMETER SPECTROMETER

The refractive indices were determined using the small angle hollow glass prism technique developed by Chatelain [2, 3] and extensively used later by Madhusudana et al [4], Shashidhara Prasad and Subramanyam et al [5], Krishnamurti et al [6], Nagappa et al [7], Somashekar et al [8],

The refractive indices were determined using Precision Goniometer S.G01.1 (Freiber ger prazision mechanik GDR). Figure 3.3 shows the Goniometer
Figure 3.1: Experimental arrangements of Leitz - polarizing microscope

Figure 3.2: Experimental arrangements of Abbe refractometer
spectrometer and the other auxiliary equipment used for the measurements. This spectrometer is quite similar to any other ordinary spectrometer, but has some special features built into it, making it a convenient and precision instrument.

The accuracy of this spectrometer is two seconds of an arc. The alignment of the spectrometer, the prism table, collimation and focusing the telescope are carried out as usual. When the director (optic axis) of the liquid crystalline sample inside the prism is parallel to the refracting edge of the prism, we observe two different spectrum with one of them having its vibration direction perpendicular to the length of the refracting edge and this corresponds to the extraordinary vibration and the later to the ordinary vibration. The former image having the greater angle of deviation. When the sample is observed between crossed polars, with the vibration direction of either the analyzer or polarizer along the direction of the refracting edge of the prism, complete extinction and the perfect polarization of the two images as mentioned above is the criterion for checking whether the sample is homogeneous and perfectly oriented or not.

To begin with, the sample was maintained at a temperature 2 or 3 °C below the mesomorphic-isotropic transition temperature and the refractive indices were measured by the method of minimum deviation using the well-known formula,

\[
\eta = \frac{\sin\left(\frac{A + D}{2}\right)}{\sin\left(\frac{A}{2}\right)} \quad \ldots 3.1
\]

After making measurements at one temperature the voltage across the terminals of the block is increased by about two volts so that the temperature increase by about two volts so that the temperature increase by about 3 or 4 °C. The sample is allowed to attain a steady temperature. This was repeated with a fresh sample and the average of the two independent sets of reading was taken for further analysis.
Measurement of the refractive index of the sample at a temperature exactly corresponding to the mesomorphic-isotropic transition point is very difficult. The mesomorphic-isotropic point can also be defined as that point at which the two images (i.e., due to extraordinary and ordinary rays) suddenly merge together to give a single sharp image. Therefore by slowly increasing the voltage across the terminals of the heater of the chamber, one can measure the refractive index at a temperature. The measured refractive indices are estimated to be correct to within ±0.001.

Here the experimental investigations involved the following steps.

(1) Fabrication of hollow glass prism.
(2) Construction of the hot chamber.
(3) Measurement and maintenance of uniform temperature throughout the region of the sample.
(4) Orientation of the specimen inside the hollow prism.

The details of the technique adopted with regard to the above are as follows.

3.3.3 FABRICATION OF HALLOW GLASS PRISM

To prepare hollow glass prism, clear optically plane glass plates were obtained from M/S National Scientific Instruments Limited, New Delhi, India. They were cut to a suitable size viz. 1.5 x 1.0 cm². Using auto collimation system available in a Goniometer spectrometer model for testing the parallelism of the planes of the glass plates. Here, one makes use of the fact that when two surfaces of the plate are plane and parallel, the reflected image from the front and the back surfaces of the plate will overlap.

Using such plates of uniform dimensions, small angle prisms of different angles were prepared using araldite, local adhesive that does not react with the sample. Before fabrication, the edges of the glass plates to be cemented together were well ground with silicon carbide in order to achieve an excellent bonding. Assuming the refractive index data (for 5893 Å) for few standard liquids, the
prism angle was computed using the equation 3.1. The prism angle was of the order of 4 to 5°.

3.3.4 CONSTRUCTION OF THE HOT CHAMBER

The birefringence of liquid crystalline compound is strongly temperature dependent. Hence, in order to maintain the specimen temperature at any desired values, a special hot chamber was constructed and this is shown in Figure 3.4(a). The prism could be easily positioned inside the hot chamber through a side hole. There are two other holes for the entry to and exit of the incident and refracted light. The prism is justaposed with the thermocouple junction and was wrapped with copper foils. The outer surface of the copper block was covered with thin mica sheets over which nichrome wire was wound. The nichrome wire (resistance nearly 300 ohms) was wound in several layers with mica insulation between adjacent layers. The entire assembly was kept in a wooden chamber and the empty space between the wooden chamber and the central block was filled with a paste of asbestos powder. The two ends of the nichrome wire connected to the two terminals $T_1$, $T_2$ to which a variable AC voltage from an autotransformer was applied. The transformer was provided with a voltage regulator on the primary side. A study of the variation of the temperature with voltage was made using a calibrated copper-constantun thermocouple. To attain a temperature of about 150°C it was necessary to apply a voltage 95 V.

3.3.5 MEASUREMENT AND MAINTAINANCE OF UNIFORM TEMPERATURE THROUGHOUT THE REGION OF THE SAMPLE

Temperature measurements were carried out using a thermocouple. It was calibrated using the standard value of melting point of pure compound such as salicylic acid. The measured values of temperature using the thermocouple were in agreement to with in ± 0.2 °C with the standard. The temperature of the hollow
glass prism inside the hot chamber and its immediate surroundings were allowed to attain an equilibrium value by waiting for about one hour before carrying out measurements. Under these conditions, the temperature fluctuation over the region of the sample was kept within ±0.2 °C. This fluctuation was in effect of changing the refractive index value only in the fourth decimal place of about ± 0.0002.

3.3.6 ORIENTATION OF THE SPECIMEN INSIDE THE HALLOW PRISM

Liquid crystalline materials inside the prism were oriented (a) by continuously rubbing the inner surfaces of the prism with thin and very clean paper strips, the rubbing direction being parallel to the length of the refracting edge of the prism and (b) by allowing a small amount of the pure sample in the liquid phase to flow slowly into the prism from the top along its refracting edge. Thus it was possible to obtain a homogeneously oriented specimen with the optic axis parallel to the refracting edge of the prism i.e. parallel to the rubbing direction and this is cross checked by marked polarizer. The preparation of a homogeneously oriented sample inside the prism is quite difficult. This can be achieved by slow cooling from isotropic to the crystalline phase in the presence of a strong magnetic filed (of the order of 10,000 gauss). In the absence of crystals at room temperature, it was not possible to gather any data in the crystalline phase. Figure 3.4(b) shows the glass prism containing the sample near the refracting edge.

3.4 EXPERIMENTAL DETERMINATION OF THE DENSITY OF THE LIQUID CRYSTAL

Density data are essential for calculation of the polarizabilities from the refractive index data [9]. The density is determined by measuring the length of the specimen inside a capillary tube for different temperature. To study the
Figure 3. Schematic diagrams of (a) The hot chamber. (b) The prism with sample.
temperature variation of density, a special electrically controlled hot chamber was used. The capillary tube containing the sample was kept inside the hot chamber. The tube was enclosed all around by thin copper foil (to ensure good thermal contact), leaving a small opening of only few millimeters on either side of the thread of the specimen for observation. A thermometer of 0.5 °C ranges was kept in good thermal contact with thin copper foil and it was kept at the center of the chamber close to the capillary tube. The length of the sample in the tube increases with increase of temperature in the chamber due to the thermal expansion of the sample. The actual lengths of the thread at different fixed temperatures were measured for all the compounds using a sensitive travelling microscope, which could read the lengths accurate to ± 0.001 cm. The mass of the thread was earlier determined using a single pan electronic microbalance, which could read the mass in grams accurately correct to the fourth decimal place. The experimental arrangement is shown in Figure 3.5 and the densities of the sample were calculated using the relation

\[ \rho = \frac{M}{\pi r^2 l} \] ...3.2

where \( l \) is the length and \( M \) is the mass of the sample thread at each temperature and \( r \) is the radius of the capillary tube at each temperature. The radius \( r \) was determined by measuring the length of the mercury thread in the same capillary tube at different temperatures and by assuming the density of mercury at these temperatures. The measured values of density are found to be accurate within ± 0.001 gm / cc.

3.5 DETERMINATION OF BIREFRINGENCE (\( \Delta n = n_e - n_o \))

To determine \( \Delta n \), the following experimental procedure was adopted. It is well known that the spectrum of white light transmitted though a system consisting of a birefringent material kept between crossed polars in found to exhibit a series of dark bands [10] satisfying the equation

\[ m x = \pi \Delta n \] ...3.3
Figure 3.3 : Experimental arrangements of Goniometer Spectrometer

Figure 3.5 : Experimental arrangements of sensitive travelling microscope used for density measurement
where \( m \) is the integer, \( t \) is the thickness of the birefringent material and \( \Delta n \) is the birefringence. The order of interference \( m \) is determined by

1. measuring the different wavelengths extinction,
2. preparing a strip chart of \( \log \lambda \) and \( \log m \) and matching these two charts.

Thickness of the crystals were determined accurately to within ±0.0001 cm using a reflecting microscope, which has a calibrated drum to measure the two positions of focusing corresponding to the front and back surface of the crystalline plates. Using equation 3.3, \( \Delta n \) was calculated at the wavelengths corresponding to the extinction.
REFERENCES