CHAPTER - II

EXPERIMENTAL TECHNIQUES
A brief review of the principal experimental methods employed by the author for measurement of Ultrasonic velocity, Density, Refractive Index and Electron Paramagnetic Resonance is given in this chapter.

2.1 ULTRASONIC VELOCITY:

a. Introduction.

The most suitable technique for the measurement of ultrasonic velocity in liquids is the interferometer method.

In 1925, Pierce [1] used a source of continuous waves to produce standing waves between transmitting crystal and a reflector. By moving the reflector and detecting the positions corresponding to the formation and destruction of stationary sound waves, the wavelength can be estimated. The most important factor in the precise determination of this method is the parallelism between the transmitter and the reflector. Hubbard, Fox and Herzfeld and others [2-4] have provided a number of modifications from time to time.

In 1949, Fry [5] replaced the reflector by an identical transducer which acts as a receiver. Zartman and Hubbard [6] have developed fixed path double crystal interferometer to study the temperature variation of ultrasonic velocity in gases.
In 1957, Rao and Rao [7] developed a double crystal fixed path interferometer for the measurement of the ultrasonic velocity in liquids. The modified version of the above technique has been employed in the present investigations.

b. Experimental detail:

The double crystal fixed path interferometer consists of two identical quartz crystals having the same fundamental frequency, separated by distance 'L'. The R.F. voltage from the high power oscillator is applied to the transmitting crystal, which is excited into forced vibrations generating ultrasonic waves in the medium. The ultrasonic waves after passing through the medium will be received by the receiver crystal at the other end. The voltage developed across it is measured by means of a sensitive vacuum tube voltmeter. When the frequency of the driving oscillator is varied continuously, a stationary grating will be formed at the discrete frequencies and consequently there will be the corresponding maxima in the voltmeter at these positions. According to the theory of the double crystal interferometer given by Fry and Musa [5] the frequency interval '$\Delta f$' between any two consecutive maxima can be shown nearly equal to the fundamental frequency of the liquid crystal column. From this it can be shown that

\[ V = 2L \times \Delta F \]
where \( L \) is the length of the liquid crystal column. By measuring the frequency changes at every interval of 10 maxima, over a wide frequency range covering at least 100 to 150 maxima, \( \Delta F \) can be determined to a high degree of accuracy.

c. **Interferometer cell:**

The Interferometer cell and its parts are shown in Fig - II - 1 - b. The cell is a hollow stainless steel container with rectangular cross-section having outer dimension of 3 x 3 x 2.5 cms, and the wall thickness 2 mm. The capacity of the cell is around 10 c.c. A tight lid with a small opening to insert the thermocouple - leads for the temperature measurements is provided for the cell. The two opposite sides of the cell are drilled for 2.2 cms diameter holes. These two sides are machined on precision milling machine for exact parallelism to \( \pm 0.1 \) mm and ten finely polished. the X-cut quartz crystal of 2 MHZ fundamental frequency and 2.5 cms diameter, obtained from M/s Bharat Electronics Ltd., are used as a transmitting and receiving transducers. These crystals are central lay placed over the apertures and fixed with 'Araldite'. The faces of the crystals are gold plated which serve as electrodes. The shields for the crystals consists of two brass cups sufficient to cover the crystal assembly, with rim diameter of about 4 mm which presses on the stainless steel walls of the cell, also making for the earth connection. These cups are fixed to the cell by
bolts welded to the four corners each of the two opposite faces of the cell. From the microphone connector, fixed to the base of the cup runs a small spring, having a soldered electrode at the other end. When the crystal shields are set in position, the metal electrode from the spring gold plated surface of the crystal to establish the electrical contact. A brass pipe of 1 cm diameter bent into L shape is coupled to the metal cup by BNC connectors. The cable through the brass pipe is insulated by using porcelain brads. A (female) BNC connector is fixed at the end of each of the two brass pipes so as to connect them to R.F. oscillator and vacuum tube voltmeter through shielded cables provided with (male) BNC connectors, as shown in Fig: II-1-b.

d. Procedure.

The experimental procedure for the measurement of as follows. The liquid crystal is put in the interferometer cell which is covered with a lid and the cell is immersed in an oil-bath whose temperature is maintained constant by a circulating thermostat (MLW - 0.2 Germany) to the accuracy of ± 0.02 °C. The liquid crystal is heated to a temperature, about 10°C beyond its anisotropic - isotropic transition temperature and the measurements are taken while cooling of the isotropic liquid, the three units Fig: II-1-a viz the R.F. oscillator, the frequency meter and the V.T.V.M are switched on and allowed for the preliminary heating as well as to obtain thermal
equilibrium. The condensor of the oscillator is set at a certain frequency which is accurately measured by a frequency-meter. The frequency is then continously varied so as to cover 10 maxima in the V.T.V.M, at every step the frequency is noted down. The procedure is repeated to cover atleast 100 maxima. The mean value of $\Delta F$ between two consecutive maxima is calculated from the above measurements. In order to measure the velocity at various temperatures, everytime, the oil bath temperature is set by the contact thermometer of thermostat. The ultrasonic velocity is determined by substituting the value of $\Delta F$ in the relation $V = 2L \times \Delta F$ where $L$ is distance between two quartz crystals $L$ is determined accurately by measuring $\Delta F$ for atleast ten different liquids in which the accurate velocities are already known, the mean $L$ from the above measurements is the required constant. The accuracy of velocity measurements is $\pm 0.1\%$.

2.2 DENSITY:

The density measurements are carried out using a special dilatometer constructed for this purpose. The dilatometer consists of a pyrex bulb of capacity of approximately one 1 cc. A capillary tube of length 25 cm and bore diameter 0.5 mm is fused to the bulb on one side which allows the introduction of the liquid crystals into the dilatometer. The aperture is closed using an air tight cork. The oil bath is a
THERMOMETER
APPARATUS FOR DENSITY MEASUREMENT

FIG. II-2-1
APPARATUS FOR DENSITY MEASUREMENT
three litre beaker containing liquid paraffin. The beaker is kept in an enclouser to avoid rapid cooling by radiation. The bath is placed over a magnetic stirrer with hot plate and an iron capsule stirs the bath as desired Fig: II - 2 - 1. A precision thermometer is immersed in the bath for temperature measurements. The rise of liquid in the dilatometer measured using a cathetometer first the empty dilatometer is weighed using electronic microbalance. It is then filled with the liquid crystal up to a fixed mark at the stem of the capillary and is weighed again. The cork is closed and coated by a film of 'Araldite'. The dilatometer is then immersed in the bath such that the mouth of the capillary tube remains above the liquid level. The bath is then heated as well as stirred continuously. The electric heater controlled by dimmerstate has been immersed in the bath. The liquid crystal is heated to about 15°C beyond the mesophase isotropic transition temperature. The bath is then allowed to cool at a rate of 4°C per hour. The cathetometer is focussed on the lower meniscus of the liquid-crystal column of the capillary and the readings are taken at an interval of 10°C in the anisotropic and isotropic phases away from transition and at an interval of 0.2 to 0.5 in the vicinity of the phase transition. The volume of the liquid crystal is computed at different temperatures and knowing the mass and volume the densities are calculated. The density measurements are accurate to ± 0.0001 gm/cc.
2.3 REFRACTIVE INDEX :

(a) Introduction

The refractive index of liquid crystals were usually measured by critical angle refractometers such as Abbe or Pulfrich refractometers. These refractometers have to be modified such that they have a proper glass prism possessing the refractive index higher than that of liquid crystals. Ordinary laboratory spectrometers suffer from the disadvantage of the low resolution of the telescope and inaccuracy of the vernier to give absolute or relative values of the index of the material under study. Hence a modified laboratory spectrometer of low cost with easy operation is prescribed, which can be used to measure the refractive indices of highly viscous liquids with no upper limiting value and a good accuracy.

(b) Design and Construction :

In order to avoid the difficulty of measuring refractive index of liquid crystal we have not preferred using commercially available refractometers (Abbe and Pulfrich), instead, installed some discrete parts such as an objective with long focal length, and ocular scale etc. Fig: II - 3 - 1 shows the construction details of the telescope. It consists of long focal length objective (f = 40 cm. aperture = 45 cm) and a measuring unit of a reflecting prism is arranged on the optic
axis for convenience to observe the images in the horizontal plane instead of vertical plane. The measuring unit of lateral moment of transmitted beam consists of (a) Cursory like; which can be called an index line (thickness = 10 um) mounted to infer the zero-zero coincidence of index line and the drum beam reading. (b) Scale mount consisting calibration ocular scale of 50 divisions each corresponding to one minutes which can be moved laterally (i.e. horizontal plane of the prism table) over the fixed index line by using the drum head. (c) Drum head consisting of 40 divisions which is attached to the ocular sale. The 40 division on the rum head correspond to one minute in the ocular scale i.e. each division of drum head is equal to 1.5 seconds of arc. The ocular scale is fixed in a brass block which is machined as a dove tail, and dove tail lateral movements are made with a pointer through a bush, from the drum head attached to a screw with spring action on the other dove tail. Thes scale can be viewed through the eye piece (20 X).

The absolute accuracy in refractive index, N = ± 0.0004 for the above cell. The advantage in using ocular scale is elimination of the personal as well as mechanical error.

(C) Determination of Refractive Index:
The refractive index is determined by the thin prism formula

\[ n = (1 + \frac{D}{A}) \]
where \( D \) = deviation.

\[ A = \text{angle of prism or angle of wedge shape cell.} \]

Deviation \( D = \left[ \text{ocular scale reading} \times 40 \text{ sec} \right] + \left[ \text{drum head reading} \times \text{least count (2 sec)} \right] \).

The position of the slit image on the ocular scale without the cell is noted. The position of the slit image after introducing the cell is recorded, the difference being equal to the deviation. By changing temperature and using the above formula \( n_0 \), the ordinary refractive index and \( n_e \), the extraordinary refractive index can be measured.

2.4 ELECTRON PARAMAGNETIC RESONANCE (EPR):

The experiments were performed on a Varian E-109 spectrometer equipped with variable temperature accessory. Sample containing cholestane probe (\( 10^{-3} \) M) contained in a quartz tube of outer diameter 5 mm. This was held in goniometer attached to the cavity of the Varian 109 EPR spectrometer. The temperature was measured with a copper constantan thermocouple inside the tube. The permitted temperature control was ± 0.5 °C. Nematic mesophase were oriented by 3.3 KG working field. The value of hyperfine splitting below N-I transition temperature is used to find orientation order parameter.

2.5 SYNTHESIS OF LIQUID CRYSTALS:

The present investigations include the three members of a homologous series.
p-(p'-n alkoxybenzoyloxy) anisole viz.
1. p-(p'-n heptyloxybenzoyloxy) anisole (HBA)
2. p-(p'-n octyloxybenzoyloxy) anisole (OBA)
3. p-(p'-n decyloxybenzoyloxy) anisole (DBA) and
4. p-(p'-n decyloxybenzoyloxy) bezaldehyde (DBB)

There are three steps involved in the preparation of these specimens

(a) **Preparation of p-n alkoxybenzoic acid.**

p-hydroxybenzoic acid (0.1 mole) is dissolved in a solution of potassium hydroxide in 100 ml ethanol. The alkyl (heptyl/octyl/decyl) bromide (0.11 mole) was added to the above solution and the mixture is refluxed for eight hours. After refluxing the mixture is treated with ice and hydrochloric acid. The alkoxybenzoic acid separate out as precipitates. This is then filtered and recrystallised using absolute ethanol. This is repeated several times till the same transition temperature is recorded.

(b) **Synthesis of p-n alkoxybenzoyl chloride**

p-n alkoxybenzoyl chloride is prepared by treating the p-n alkoxybenzoic acid (0.1 mole) with thionyl chloride (0.15 mole). The resulting solution is refluxed for six to eight hours so that it is devoid of any HCl or SO₂. The excess thionyl chloride is also removed by distillation.
Synthesis of \( p^- (p' - n\ \text{alkoxybenzoyloxy}) \) anisole and \( p^- (p' - n\ \text{decyloxybenzoyloxy}) \) benzaldehyde:

To a solution of \( p^- \text{methoxy phenol} \) (0.1 mole) in dried pyridine is added \( p^- \text{alkoxybenzoic acid} \) (0.1 mole) the mixture is then stirred at room temperature for two hours and kept over night. Then is acidified with cold dilute HCl. The resulting precipitations of ester are filtered off and washed with ethanol to remove pyridine. The product is then recrystallised several times with absolute ethanol till it gives constant transition temperature.

The \( p^- (p' - n\ \text{decyloxybenzoyloxy}) \) benzaldehyde is synthesised same way as mentioned above only difference is instead of \( p^- \text{methoxy phenol} \) the (0.1 mole) \( p^- \text{hydroxy benzaldehyde} \) has been used.

2.6 TRANSITION TEMPERATURES AND TEXTURES:

The best instrument to be used for the determination of the transition temperatures and identification of the textures of liquid crystals is the polarizing microscope; equipped with a electrically controlled hot plate stage. The microscope used in these investigations is a Leitz Laborlux - II Pol./Binocular polarizing microscope equipped with heating stage Fig. II - 6 - a. The temperatures for the heating stage are electracally controlled by a regulator, in range from room temperature to
PLATE - 1: SCHLIEREN TEXTURE OF THE NEMATIC PHASE.

PLATE - 2: FOCAL CONIC TEXTURE OF THE SMECTIC - A PHASE.
PLATE 3: FOCAL CONIC FAN TEXTURE OF THE SMECTIC - B PHASE.

PLATE 4: PLANE TEXTURE OF THE CHOLESTERIC PHASE.
360°C and can be conveniently read out by suitable thermometers. The heating stage calibration has been done using standard specimens. The transition temperatures and the various textures of mesophase are clearly observed and recorded in the polarized light. The transition to the isotropic liquid is clearly marked when the field of vision becomes extinct in the polarized light. The transition temperatures recorded in the present investigations are accurate to ± 0.1°C.
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