CHAPTER - II

EXPERIMENTAL TECHNIQUES

The details of the experimental techniques employed by the author during his work are included in this chapter. For the measurements of ultrasonic velocity, the double crystal fixed-path interferometer technique has been employed. Abbe refractometer has been used for the measurements of refractive indices. For the measurements of density, a specially constructed dilatometer has been used. The details of these experimental sets-up have been discussed here.

INTERFEROMETER TECHNIQUE :

The first single crystal interferometer method was developed by Pierce[1]. In this interferometer, the source produced the continuous waves is used to create standing waves between the transmitting crystal and the reflector. Pierce had used an X-cut quartz crystal as a transducer which was excited by an R.F oscillator. A plane reflector was set accurately parallel to the transducer at a distance which can be adjusted by a micrometer arrangement. As the reflector wasmoved, it passed through the resonance and antiresonance positions causing the reaction on the quartz cyrstal, thereby showing the maximum and minimum currents. Recording the plate current of the driving oscillator for different settings of the reflector, the velocity and the absorption coefficients can be determined. In the double crystal interferometer, Fry [2] has replaced the reflector by an identical transducer which acts as areceiver. In this method the received output amplitude will go through

maxima and minima as the separation of the transducer is varied. The spacing between adjacent maxima will be very nearly equal to half a wavelength. For precision velocity measurements the effect of attenuation will have to be considered. Rao and Rao [3] have developed a double crystal fixed path interferometer to measure the ultrasonic velocity in liquids. This method has certain advantages over the other methods. As the name implies, in this method, the distance between the transmitting transducer and receiving transducer is fixed, thus overcoming the practical difficulty of moving the receiving crystal exactly parallel to the transmitting crystal. The frequency of the high power oscillator exciting the transmitting crystal is varied continuously, thereby varying the wavelength of the sound waves in the medium. At certain descrete frequencies the liquid column will be in resonant vibrations and correspondingly there will be peaks in the voltmeter connected to the receiving crystal. This method has been employed by the author to measure the ultrasonic velocity.

PRINCIPLE OF THE DOUBLE CRYSTAL FIXED-PATH INTERFEROMETER:

The double crystal fixed path interferometer consists of two identical quartz crystals having the same fundamental frequency, separated by a distance 'L' with the liquid medium between them. The R.F voltage from the high powered 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 and the voltage developed across it is measured by means of a vacuum tube voltmeter. When the frequency of the driving oscillator is varied continuously, a stationary grating will be formed at the descrete frequencies and consequently there will be the corresponding maxima in the voltmeter at these transitions. From the theory of the double crystal interferometer given by Fry and Musa [4] the frequency interval 'Δf' between any two consecutive maxima can be shown nearly equal to the fundamental frequency of the liquid column and from this it can be shown that,

$$V = 2L \times \Delta f$$

where 'L' is the length of the liquid column. By measuring the frequency changes at every interval of 10 maxima, over a wide frequency range covering at least 100 to 150 maxima, Δf can be determined to a high degree of accuracy.

MEASUREMENT OF ULTRASONIC VELOCITY:

The block diagram of the experimental set up is represented in Figure 2.1. It consists of a variable frequency oscillator (frequency range 1 MHz to 3 MHz), the acoustic cell with shielded crystal holders and a sensitive vacuum tube voltmeter. The circuit diagram of the variable frequency oscillator with regulated power supply is given in Figure 2.2. It consists of 6L6 beam power tetrode employed in a conventional shunt-fed Hartley circuit. The entire oscillator is enclosed in a

shielded metal box provided with sufficient ventillation for the heat dissipation of the valves. The R.F voltage is applied through a sheilded cable to the transmitting crystal of the cell. The voltage developed across the receiver crystal is measured by a sensitive A.C millivoltmeter (Simpson, model 727-I), which acts as a wide band amplifier enabling direct measurements upto 0.1 millivolt. To avoid any stray pick up in the voltmeter, the output of the receiver crystal is connected to the input of the V.T.V.M. through a shielded cable. The precise measurement of frequency is carried out by a digital frequency meter (Aplab, model 1102), whose accuracyis 1 in 10^{-6}.

The interferometer cell and it's parts are shown in Figure2.3. The cell is a hollow stainless steel container with rectangular cross-section having dimensions of 3x3x2.5 cms, and wall thickness of 2mm. The capacity of the cell is around 20 cc. A tight lid having a small opening to insert the thermocouple leads for the temperature measurement is provided with the cell. The two opposite sides of the cell are drilled for the holes of 2.2 cms diameter. These two sides are machined on precision milling machine for exact parallelism to ±0.2mm and then finely polished. Two X-cut quartz crystals of 2 MHz fundamental frequency and 2.5 cms diameter, obtained from M/s Bharat Electronics Ltd., are used as transmitting and receiving transducers. These crystals are centrally placed

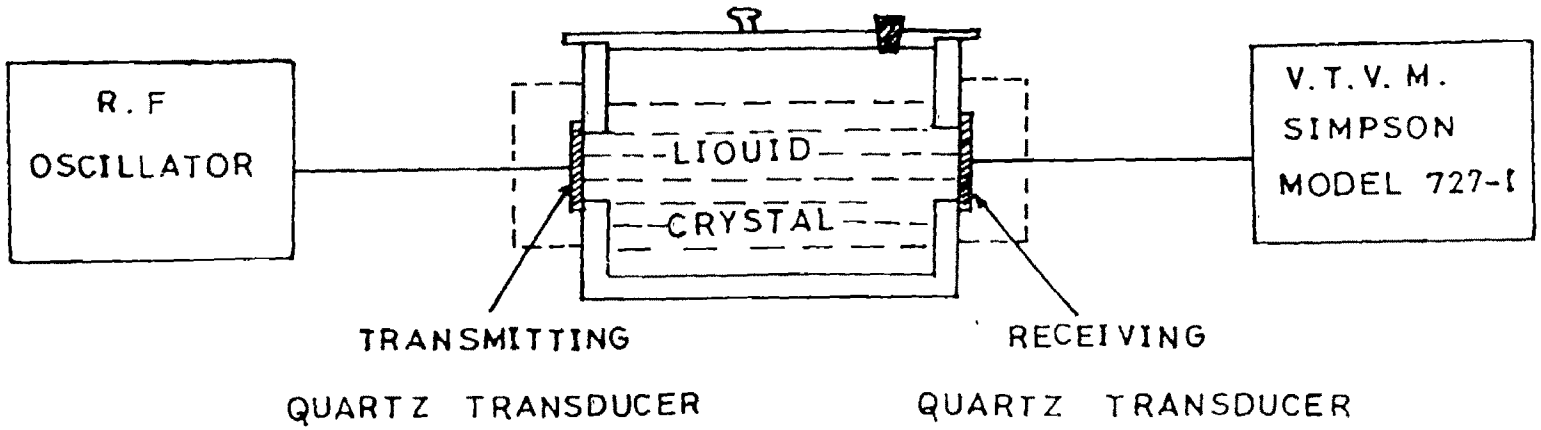

FIG. 2.1: BLOCK DIAGRAM OF CONTINUOUS WAVE ELECTRICAL METHOD

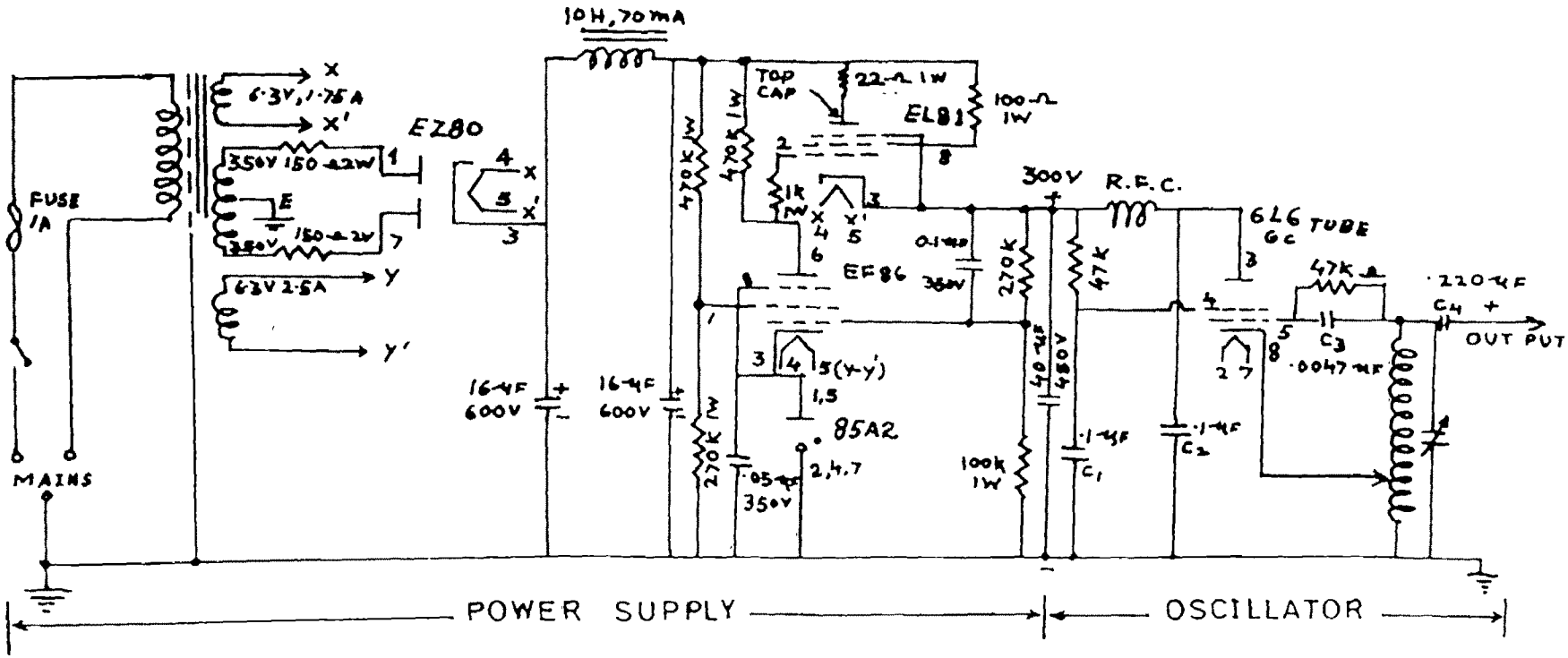

FIG. 2.2 : CIRCUIT DIAGRAM OF POWER SUPPLY AND R.F. OSCILLATOR

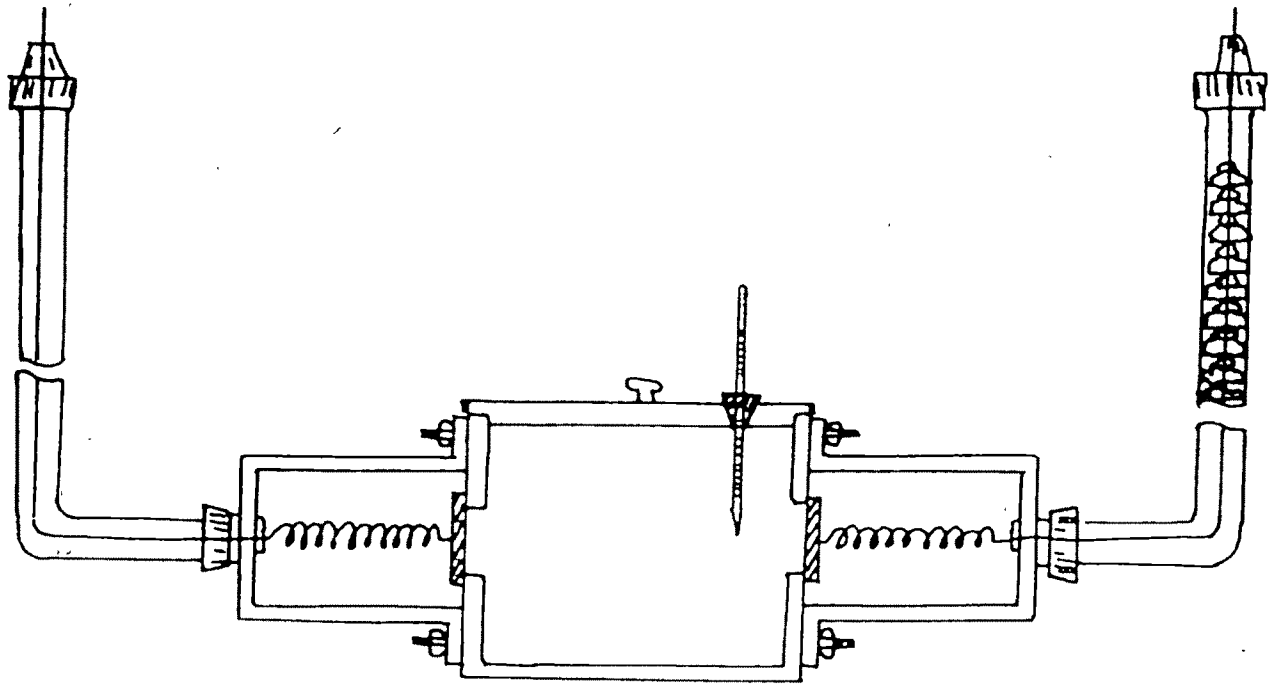

FIG. 2.3: DETAILS OF CELL AND CRYSTAL HOLDER

(NOT TO SCALE)

over the apertures and fixed with 'araldite'. The faces of the crystals are gold plated which serve as electrodes. The shields for the crystals consist of two brass cups sufficient to cover the crystal assembly, with the rim diameter of about 4mm 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 ofthe cell. From the microphone connector, fixed to the base of the cup runs small spring, having a soldered electrode at the other end. When the crystal shields are set in position, the metal electrodes from the spring touch the 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 microphone connectors. The cable through the brass pipesis insulated by using porcelein beads. A (female) microphone connector is fixed at the end of each of the two brass pipe so as to connect them to R.F. oscillator and thevacuum tube voltmeter through shielded cables provided with (male) microphone connectors as shown.

The experimental procedure for the measurement of velocity is as follows. The liquid crystal is taken 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-U2, Germany) to the accuracy of ±0.02°C The liquid cyrstal is heated to a temperature, about

10°C beyond it's mesomorphic-isotropic transition temperature and the measurements are taken while cooling of the isotropic liquid. The three units, the R.F oscillator, the frequency meter and the V.T.V.M are switched-on and some time is allowed for the preliminary heating as well as to obtain the thermal equilibrium. The condenser of the oscillator is set at a certain frequency which is accurately measured by a frequency-meter. The frequency is then continuously varied so as to cover 10maxima, in the V.T.V.M, every step noting down the frequency accurately. The procedure is repeated to cover atleast 100 maxima. The mean value of '$\triangle$f' between two consecutive maxima is calculated from the above measurements. In order to measure the velocity at various temperatures, every time, the oil bath temperature is set by the contact thermometer of thermostat. The ultrasonic velocity is determined by substituting the value of '$\triangle$f' in the relation $V=2Lx\triangle f$, where 'L' is the distance between the two quartz crystals. 'L' is determined accurately by measuring '$\triangle$f' for at least six 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 ±0.1%.

MEASUREMENTS OF REFRACTIVE INDICES:

The refractive indices of liquid crystals are 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. Here 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 such as liquid crystals with no upper limiting value and a good accuracy.

Design and Construction:

The refractometer employed by the author has been modified to avoid any difficulty of measuring the refractive indices of liquid crystals and provide satisfactory accuracy. Some discrete parts have been installed such as an objective with long focal length and ocular scale. The telescope consists of focal length objective (f=40 cm and aperture=45 cm) and a measuring unit of a reflecting prism is arranged on the optic axis for the 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 cm) mounted to infer the zero-zero coincidence of index line and the drum beam reading. (b) scale mount consisting of calibration ocular scale of 50 divisions each corresponding to one minute 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 scale. The 40 divisions of the drum head correspond to one

minute in the ocular scale i.e each division of the drum head is equal to 1.5 seconds of the arc. The ocular scale is fixed in a brass block which is machined as a dove tail, and the dove tail lateral movements are made with pointer through a bush, from the drum head attached to a screw with spring action on the other dove tail. The scale can be viewed through an eye piece (20x). The absolute accuracy in refractive index is N=±0.0004 for the above cell.

Determination of Refractive Index :

The refractive index is determined by the thin prism formula $n = (1 + D/A)$

where D = deviation i.e ocular scale reading x 40 seconds + drum head reading x least count.

A = angle of prism or angle of Wedge shape cell.

The position of the slit 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 variaing the temperatuere the ordinary (n_o) and extraordinary (n_e) refractive indices are measured at different temperatures.The temperature variation was sensed by coper constantant thermocouple.

DENSITY:

The density measurements were carried out using a special dilatometer constructed for this purpose. The dilatometer consists of a pyrex bulb of a capacity of 1 c.c approximately.

A capillary tube of 25 cm length and above diameter of 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 for varying the temperature, the dialtometer is kept in a beaker of liquid paraffin. The beaker is kept in an encloser to avoid rapid cooling by radiation. The liquid paraffin bath is placed over a magnetic stirrer with hot plate and an iron capsule stirrs the bath for uniform heating or the system. A precision Thermometer is immersed in the bath for temperature measurements. The rise of the liquid crystal in the dilatometer is monitored using a cathetometer. First the empty dilatometer is weighed using Mettler microbalance. It is then filled with the liquid crystal upto a fixed mark at the stem of the capillary tube and is wieghed again above the liquid level. The cock 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 isthen heated as well as stirred continuously. To attain higher temperatures, an electric heater connected through a dimmerstat is immersed in the bath. The liquid crystal is heated to about 15°C beyond the isotropic-mesophase 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 column of the capillary and the readings are taken at an interval of 1°C in the isotropic and mesophase phases away from

the transition and at a closer interval at the vicinity of the transition. The density of the liquid crystal is then computed at different temperatures. The density measurements are accurate ± 0.0001 gm/cc.

ELECTRON PARAMAGNETIC RESONANCE (EPR):

The experiments were performed on Varian E-109 spectrometer equipped with variable temperature accessory. The sample containing Cholestane prob (10^{-3} M) filled in a quartz tube of outer diameter of 5 mm. This was held in a goniometer attached to the cavity of the Varian. The temperature was measured with a copper constantant thermocouple inside the tube. The permitted temperature control was ±o.5°C. Nematic mesophases were oriented by 3.3 K G working field. The value of hyperfine splitting below the isotropic - mesophase transition temperature was used to find the orientational order parameter.

SYNTHESIS OF LIQUID CRYSTALS:

The present investigations include three members of a homogeneous series and two members of the same series but with different terminal substituents. The liquid crystals which are the subject of our investigations were synthesised in our laboratory. The liquid crystals are

1. p - (p' - n pentyloxybenzoyloxy) nitrophenol (PBNP)
2. p - (p' - n hexyloxybenzoyloxy) nitrophenol (H6BNP)
3. p - (p' - n hepyloxybenzoyloxy) nitrophenol (H7BNP)
4. p - (p' - n heptyloxybenzoyloxy) benzaldehyde (HBB)

5. p - (p' - n octyloxybenzoyloxy) benzaldehyde (OBB)

The steps involved in the synthesis of these liquid crystals are

a) Preperation 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 member (pentyl/hexyl/heptyl) bromide (0.11 mole) was added to the above solution and the mixture is reflexed for eight hours and then kept overnight. The mixture is then treated with cold hydrochloric acid, and so the alkoxybenzoic acid seperates out as precipitates. This is then filtered and recrystalized using absolute ethanol. This is repeated several times till the same melting point is recorded.

b) Synthesis of p-n alkoxybenzoyl Chloride:

p-n alkoxybenzoyl chloride is prepared by treating p-n alkoxybenzoic acid (0.1 mole) with theonyl chloride (0.15 mole). The resulting solution is reflexed for six to eight hours so that it is devoid of any HCl or SO 2. The excess theonyl chloride is removed by distillation.

c) Synthesis of p-(p'-n alkoxybenzoyloxy) nitrophenol and p-(p'-n alkoxybenzoyloxy) benzaldehyde:

To a solution of p-nitrophenol (0.1 mole) in dry pyridine is added p-n alkoxybenzoyl chloride (0.1 mole), the mixture is then stirred at room temperature for two hours and kept overnight. The product is then acidified with cold and dilute

HCl. The resulting precipitations of ester are filtered off and washed with ethanol to remove the pyridine. The product is then recrystalized several times with absolute ethanol till it gives constant transition temperature. The same procedure is adopted in the case of p-(p'-n alkoxybenzoyloxy) benzaldehyde but instead of p-nitrophenol, p-hydroxy benzaldehyde is used.

DETERMINATION OF THE TRANSITION TEMPERATURES:

The most convenient apparatus for the determination of textures and transition temperatures of liquid crystals is a polarizing microscope equipped with an electrically heated hot stage. The microscope used in this investigation is a Leitz Laborlux-II Pol/Binocular Polarizing Microscope equipped with hot stage. The temperature of the hot stage is controlled electrically by a regulator, in the range of room temperature to 360°C and can be conveniently read by a suitable thermometer. The transition temperature and the various textures of the mesophases 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 polarized light. The transition temperatures recorded in the present investigations are accurate to ±0.1°C.

REFRENCES :

1. Pierce G.W. Proc. Amer. Arts. Sci 60, 271 (1925)
2. Fry W.J. J. Acous. Soc. Amer. 21, 17 (1949)
3. Rao K.S and Rao B.R. J. Sci. Ind. Res. 16 B, 483 (1957)
4. Fry W.J. and Musa R.S. J. Acous. Soc. Amer. 30, 215 (1958)