

Chapter 2

Experimental Methods

As discussed in the previous chapter, the glass transition phenomena is relaxational in nature, and hence, can be investigated using experimental techniques¹⁻⁹ such as Dielectric Spectroscopy, Nuclear Magnetic Resonance, Photon Correlation Spectroscopy and Differential Scanning Calorimetry (DSC) apart from Viscometry. Our principal preoccupation will be with dielectric measurements with DSC and X-ray diffraction as supporting techniques. The DSC explores various phase transitions and the structural relaxation in glassy materials. Among the other techniques mentioned above, dielectric spectroscopy is used most widely to study the rotational motion of individual molecules near and below the glass transition. The dielectric measurements that we are interested here correspond to sub-microwave range of frequencies, where quantum and phonon phenomena do not enter in any significant way, and measurements will extend down to the very low frequencies in the milli-hertz range and below, made accessible by recent developments in Instrumentation using time domain step response technique. While in the range above 10 Hz excellent bridge techniques are available, giving high accuracy in the measurements of even nearly non-polar (very low loss) materials, the general drawback of these bridge techniques is the limited range of frequencies which are attainable on any one instrument. However, with the invention of Personal computers (PCs) this is no more a problem as different bridges can be controlled by a single PC. Moreover, time domain (Fourier transform) techniques have become available commercially even

very high frequencies up to 30-40 GHz. and hence, the range of frequencies from 10 Hz-40 GHz can be covered in a short time. The principal aim of our dielectric measurements is to study the various relaxation processes in glassy systems. A combination of dielectric spectroscopy and DSC will provide an excellent information about the relaxation processes in the supercooled liquids. The dielectric relaxation technique is very well developed commercially for the frequency domain measurements in the form of extensive range of a.c. bridges with the advantage that signal-to-noise ratio is very high. For measurements in the frequency range of 20 Hz -1 MHz, commercially available HP 4284A precision LCR meter has been used. Measurements are extended upto the ultra low frequency range ($10^{-4} < f < 20\text{Hz}$) by using time domain method. The time domain technique is more economical in time at these low frequencies over the frequency domains methods. The time domain technique has been developed in our laboratory to facilitate the dielectric measurements in the ultra low frequency region. For frequencies in the range 20 Hz– 10^{-3}Hz , we have sampled the dielectric absorption currents in the time window of 0.01-1000 secs., using a digital storage oscilloscope (DSO) card DSO-2200 (Link Instruments Inc. USA), in combination with a Keithley Model No. 617 Programmable Electrometer. The complex permittivity was calculated by taking Discrete Fourier Transform (DFT) of the discharging current. However, there is a limitation in this kind of measurements, set by the resolution of the DSO card. Because of this, we are not able to determine the complete spectral characteristic at these low frequencies. However, the f_m values measured with the help of this technique are as good as that measured by the LCR bridge (Figure. 2.1).

2.1 Differential Scanning Calorimetry Measurements

DSC¹⁰⁻¹⁵ is a technique that records the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature. The DSC usually has platforms to keep the sample material and reference material

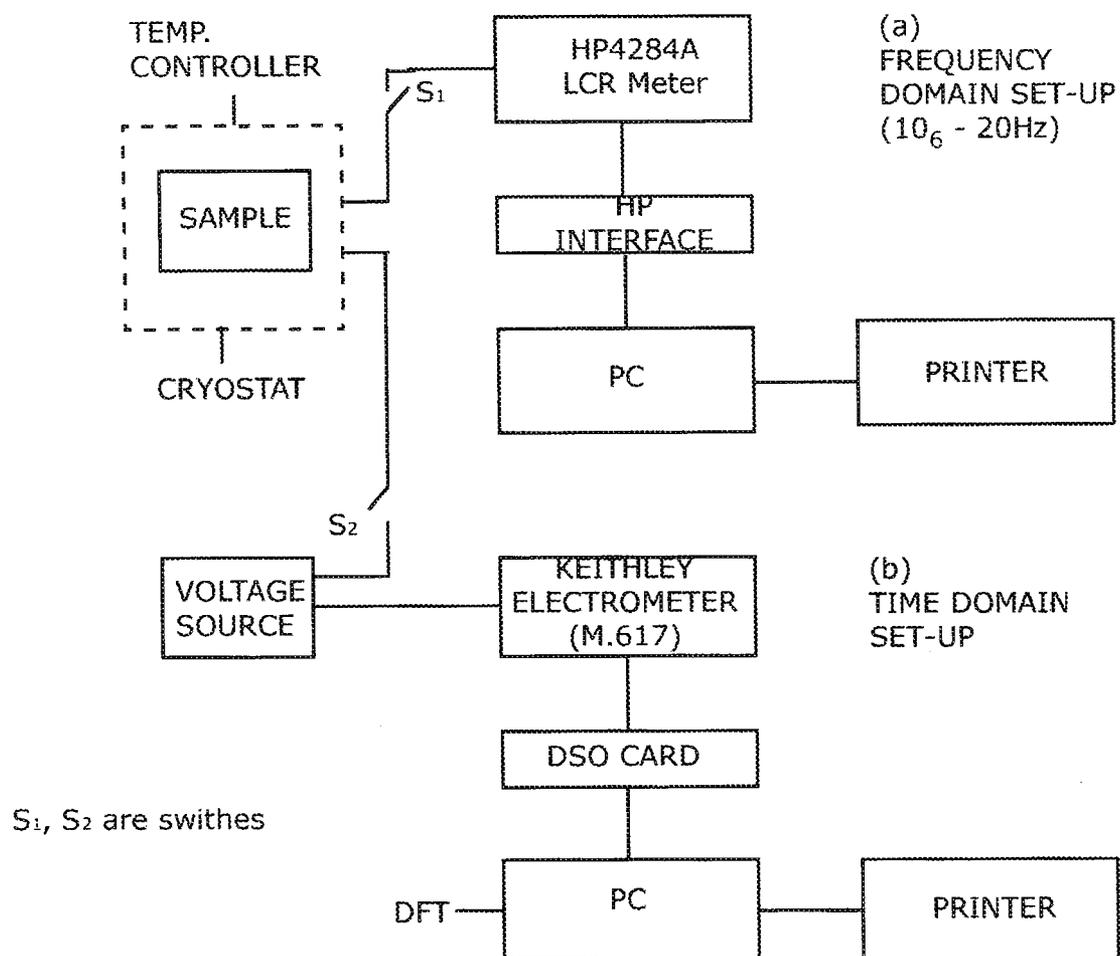


Figure 2.1: Schematic diagram of experimental set-up

taken in appropriate pans. The reference material usually chosen on the merit that it should not undergo any transition in the desirable temperature range. An endothermic thermal event (ΔH positive, such as melting) occur in the sample, the temperature of the sample, T_s , will lag behind the temperature of reference, T_r . In DSC, the sample and the reference material are maintained at the same temperature ($\Delta T = T_s - T_r = 0$) by supplying the energy difference to the sample by an independent supply and the energy difference is then recorded against the programmed temperature. Thermal events in the sample appear as deviations from baseline, in either an endothermic or exothermic direction, depending upon whether more or less energy has to be supplied to the sample relative to the reference material as shown in Figure. 2.2. A glass transition event appears as a step-like change in DSC scans (Figure. 2.2). It should be noticed that glass transition temperature depends on heating rate q as shown in Figure. 2.2 because it is relaxational in nature. A wide range of heating rates are employed in DSC experiments to explore the glass transition phenomenon.

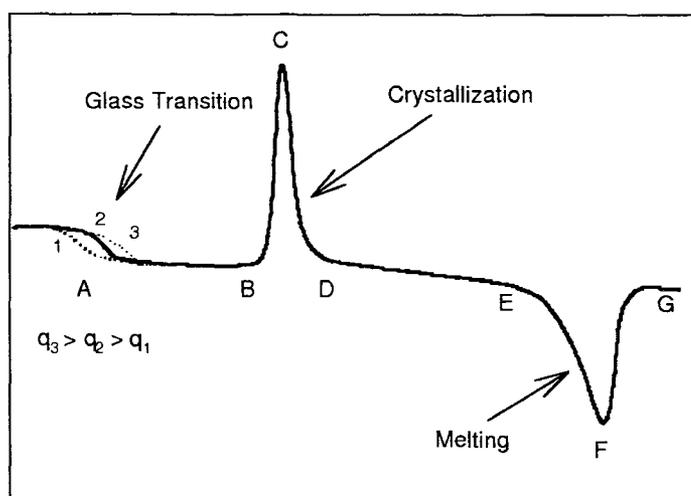


Figure 2.2: A typical DSC output showing various transitions as deviations from baseline. Curves labeled as 1, 2 and 3 correspond to heating rates of q_1 , q_2 and q_3 respectively. Note that glass transition event depends on heating rate q .

2.1.1 Description of DSC set-up

The DSC 10 system is a plug-in-module that is used with the Du Pont Thermal Analyzer 2000. (The DSC measurements reported in Chapter 6 are performed above room temperature using Perkin-Elmer DSC-7 at a heating rate of 2 deg./min. The DSC cell was calibrated for temperature using indium and zinc as the standards) The system measures the temperature and differential heat flow associated with material transitions and provides quantitative and qualitative data on endothermic and exothermic processes. The DSC 10 system consists of a cell base module, which supports the standard DSC cell. The cell base is an operating base for the DSC cell. It transmits heater voltage and thermocouple signals between the thermal analyzer and DSC cell. Output from thermocouple is controlled and amplified by circuitry in the cell base. Input ports for vacuum, cooling and purge gases, connector and calibration controls are located at the rear of the cell.

The cross sectional view¹⁴ of the DSC cell can be seen in Figure. 2.3. In the cell, the sample and reference pan sit on raised platforms on a constantan disc. Heat is transferred through the disc to the sample and reference. Differential heat flow is monitored by thermocouples located beneath the disc. The DSC cell has two separate thermocouples for sample and controlling purpose. The sample thermocouple monitors the sample temperature which is the temperature displayed on the thermal analyzer and recorded as sample temperature. The control thermocouple, is embedded in the furnace and permits precise monitoring and controlling of the heater. For cooling the sample, a quench cooling accessory is used which consists of a metal can that fits over the cell. A reservoir in the top of this can is filled with liquid nitrogen to cool the sample. For liquid and solid samples, aluminum pans have been used. The operating temperature range using aluminum pans is from 100 K to 823 K. The samples for calorimetric measurements are sealed in the pans using a sample encapsulating press.

2.1.2 Calibration of DSC

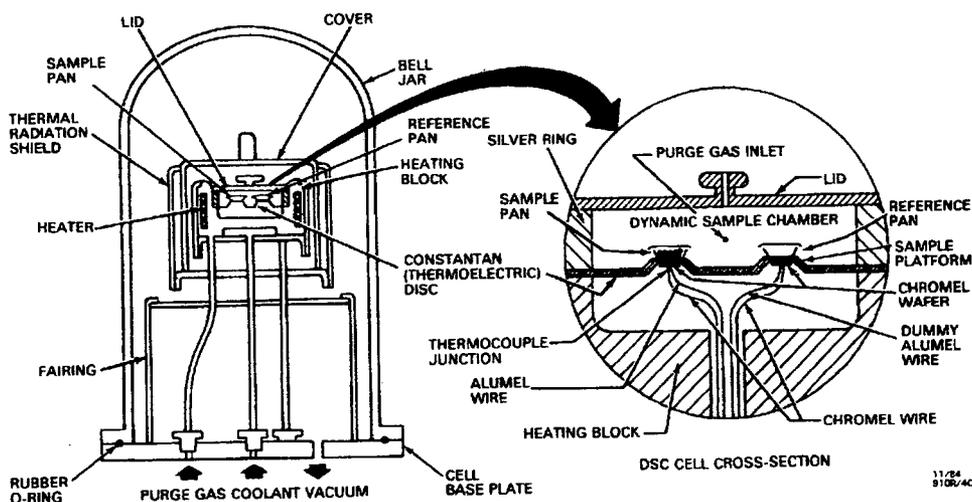


Figure 2.3: Cross sectional view of DSC cell (Ref. 12).

Calibration of sample and control thermocouples

The system is first calibrated so that both sample thermocouple and control thermocouple read temperatures correctly. The sample temperature is calibrated using a Du Pont standard two-point calibration program with indium and n-pentane as the standards. For the calibration of the control thermocouple the system is equilibrated for about 30 minutes at a set temperature so that the heater and sample are in equilibrium then the calibration control knob is rotated till the set temperature and the measured temperature (displayed as sample temperature) are identical (more details on this front are given in the instrument manual¹⁴).

Calibration of the DSC cell

The thermal analyzer provides a linear calibration coefficient (E) curve. This coefficient is constant and is usually 1.0 (dimensionless). The cell is calibrated using various standards having different melting temperatures and whose heat of fusions are known very accurately. The calibration coefficient is determined from the following formula:

$$E = \frac{\Delta H_m}{A} \quad (2.1)$$

where ΔH , m and A are heat of fusion in J/g, sample mass in g and peak area in J respectively. This procedure is repeated with various standards covering the entire temperature range of relevance and corresponding E values are measured. The standards used for this purpose are : indium ($T_m = 429.8$ K, $\Delta H_m = 3.27$ kJ/mol); naphthalene ($T_m = 80.5$ K and $\Delta H_m = 18.9$ kJ/mol); water ($T_m = 273.0$ K and $\Delta H_m = 6.01$ kJ/mol); mercury ($T_m = 234.3$ K and $\Delta H_m = 11.5$ kJ/mol). (Here suffix 'm' corresponds to the melting point.) The plot of E(T) vs T is used for the exact calculation of ΔH of transition under consideration. The accuracy of ΔH is limited by the accuracy of weighing measurements of the sample which is ± 0.1 mg.

2.1.3 Procedure For the determination of transition temperatures

A sample weighing 5-10 mg is taken in the aluminum pan and is cooled using quench cooling accessory. The time required to cool the DSC cell from room temperature down to 100 K is approximately 25 minutes, with an average cooling rate of 8 K /min. The sample is equilibrated for some time (≈ 2 -10 min.) at the lowest set temperature. Data is then taken while heating of the sample at a fixed rate. Since the quench cooling accessory does not provide high enough cooling rates required to form glass in some of the systems, the following cooling technique has been used with such samples: First the DSC cell (without sample pan) is cooled to the lowest temperature. The sample pan is dipped directly into liquid nitrogen and then it is quickly introduced into the DSC cell

at a temperature of 100 K. With this technique, the sample is cooled down to liquid nitrogen temperature in 10-15 secs, thus yielding an average cooling rate of 800 K /min. This method is used in those cases where glass formation is not possible otherwise. Though this technique causes some distortion in baseline due to moisture condensation, the baseline is usually good enough to measure the transition temperatures within experimental accuracy. The transition temperatures, at the specified heating rates are determined from the DSC curves using the software provided by the manufacturer of the instrument. Throughout this thesis the measurements reported are done on Du Pont TA 2000 system, but the measurements reported in Chapter 6 are made above room temperature using Perkin-Elmer DSC-7.

2.2 Dielectric relaxation measurements

Dielectric measurements are made in two steps. In the frequency range from 1 MHz–20Hz, measurements are made with the help of a precision Hewlett Packard HP4284A precision LCR meter bridge. In the ultra low frequency range ($10^{-0.5}$ - 10^{-3} Hz), a dc step response technique incorporating Keithley 617 Programmable Electrometer is used (Figure. 2.1). The problem of slow switching has been eliminated in some experiments using fast electronic switches (Supertex. Inc.) and the transient current data has been sampled at a very high rate using DSO-2200 oscilloscope, consequently, filling the frequency gap of 20Hz - $10^{-0.5}$ Hz.

2.2.1 Bridge technique

For the measurements of real and imaginary parts of complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$), the measurements are performed in $C_p - D$ mode of the LCR meter. In $C_p - D$ mode of LCR meter, the sample is represented as a parallel combination of capacitor C_p and resistance R_p . A sinusoidal voltage of angular frequency $2\pi f$ (f is frequency in Hz) is applied between the electrodes of sample and the net current passing through

the sample is measured. The root mean square components of current in phase I_{ph} and the one 90° out of phase I_{ou} with the applied voltage are measured by a phase sensitive detection technique. The component in phase is proportional to the conductance of the sample under test and the other one to $2\pi fC$ value. The ratio of these two currents gives 'tan δ ' value which is called dissipation factor D of the capacitor.

$$D = \frac{I_{ph}}{I_{ou}} = \frac{1}{2\pi f R_p C_p} \quad (2.2)$$

and

$$2\pi f C_p = I_{ou}/V \quad (2.3)$$

where, V is the a.c. voltage. Capacitance C_p and dissipation factor D are computed from the measured I_{ph} and I_{ou} components using applied voltage (V) and frequency f . The values displayed on screen and are simultaneously stored on computer using a GPIB card with the help of a program written in HP VEE language.

2.2.2 D.C. step - response technique

In this method¹⁵, the sample capacitor is charged by applying a d.c. step voltage (V_0), which, on fully charging is discharged by short-circuiting the capacitor. The charging and discharging currents are sampled with the help of a Keithley Programmable Electrometer (Model 617). The calculation of complex permittivity constant ϵ^* from discharging current can be done as follows.¹⁶ For a sample with geometrical capacitance C_0 , subjected to a time dependent voltage $V(t)$, the corresponding charge $Q(t)$ for a linear dielectric is given by,

$$Q(t) = C_0 \left[\epsilon_\infty V(t) + \int_{-\infty}^t dt' \Phi(t-t') V(t') \right] \quad (2.4)$$

where ϵ_∞ is the limiting permittivity and Φ is a response function. When a step voltage $V(t) = 0$ ($t < 0$), $V(t) = V_0$ ($t > 0$) is applied to the sample, the transient current $I(t)$ is given by,

$$I(t) = \frac{dQ}{dt} = C_0 V_0 [\epsilon_\infty \delta(t) + \Phi(t)] \quad (2.5)$$

The response function $\Phi(t)$ is related to complex permittivity ϵ^* by,

$$\epsilon^* = \epsilon_\infty + L\Phi(t) \quad (2.6)$$

where,

$$L\Phi(t) = \int_0^\infty \exp(-j\omega t)\Phi(t)dt \quad (2.7)$$

From Eqs. 2.4–2.6, we get

$$\epsilon^* = \frac{1}{C_0V_0} L[I(t)] \quad (2.8)$$

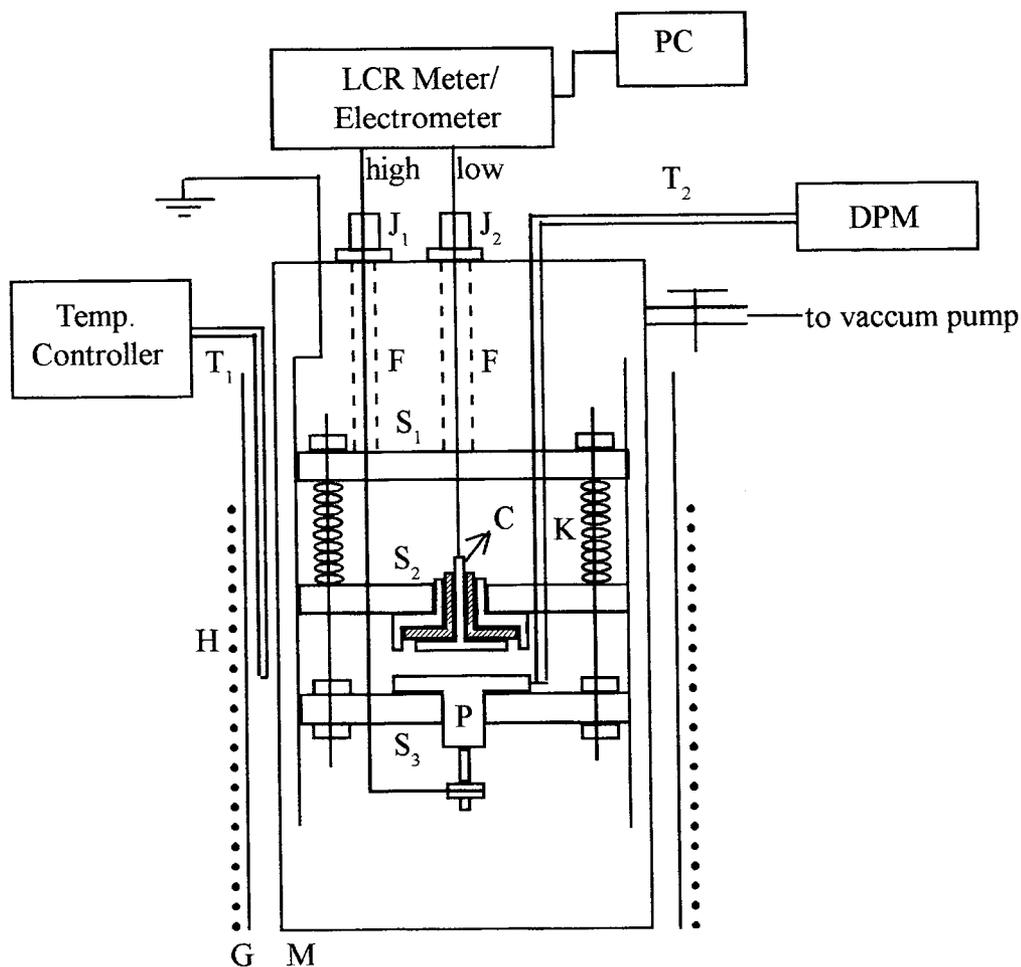
Thus, complex permittivity can be obtained by taking Fourier Transformation of the transient current. Discrete Fourier Transformation of transient current is done by a computer program.

2.2.3 Description of dielectric set-up

For the low temperature measurements a stainless steel cryostat has been used (Figures. 2.4, 2.5). The lower part and upper part of this cryostat has been separated by a Teflon connector to avoid water condensation on the upper part of the cryostat. The lower portion of the cryostat is dipped into liquid nitrogen kept in a Dewar flask.

The upper part contains two ports (input and output) which are used for gas purging. Shielded co-axial cables have been used for various connections from the dielectric cell to the measuring units to reduce the noise.

The complete set-up for low temperature dielectric measurements is shown in Figures. 2.4, 2.5. Similar set-up have been used for temperatures above room temperature. Two types of dielectric cells have been used mainly for our samples which are described below: (i) For the liquid samples¹⁷ a three terminal co-axial cell with guarded arrangement has been used. Teflon spacers have been used to separate inner electrodes (Figure. 2.4). The empty cell capacitance achieved is usually around 45 pF. The Copper-Constantan thermocouple is placed deep inside liquid to measure the sample temperature through Digital Panel Meter (DPM).



- C - guarded electrode
 P - un-guarded electrode
 M - metal shield
 H - heater
 ▨ insulating material (Teflon)
- J₁, J₂ - Amphenol connectors
 S₁, S₂, S₃ - insulating supporters (Teflon)
 F - coaxial pipe line
 K - light weight springs

Figure. 2.5(a): Dielectric measurement set-up for powdered samples in the form of pellets.

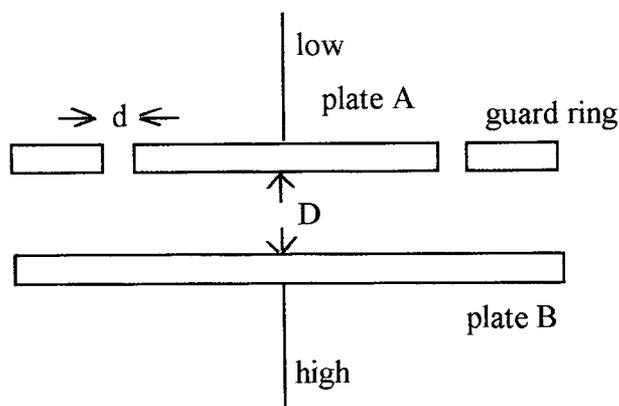


Figure. 2.5(b): Schematic diagram of a parallel plate capacitor with guard ring arrangement.

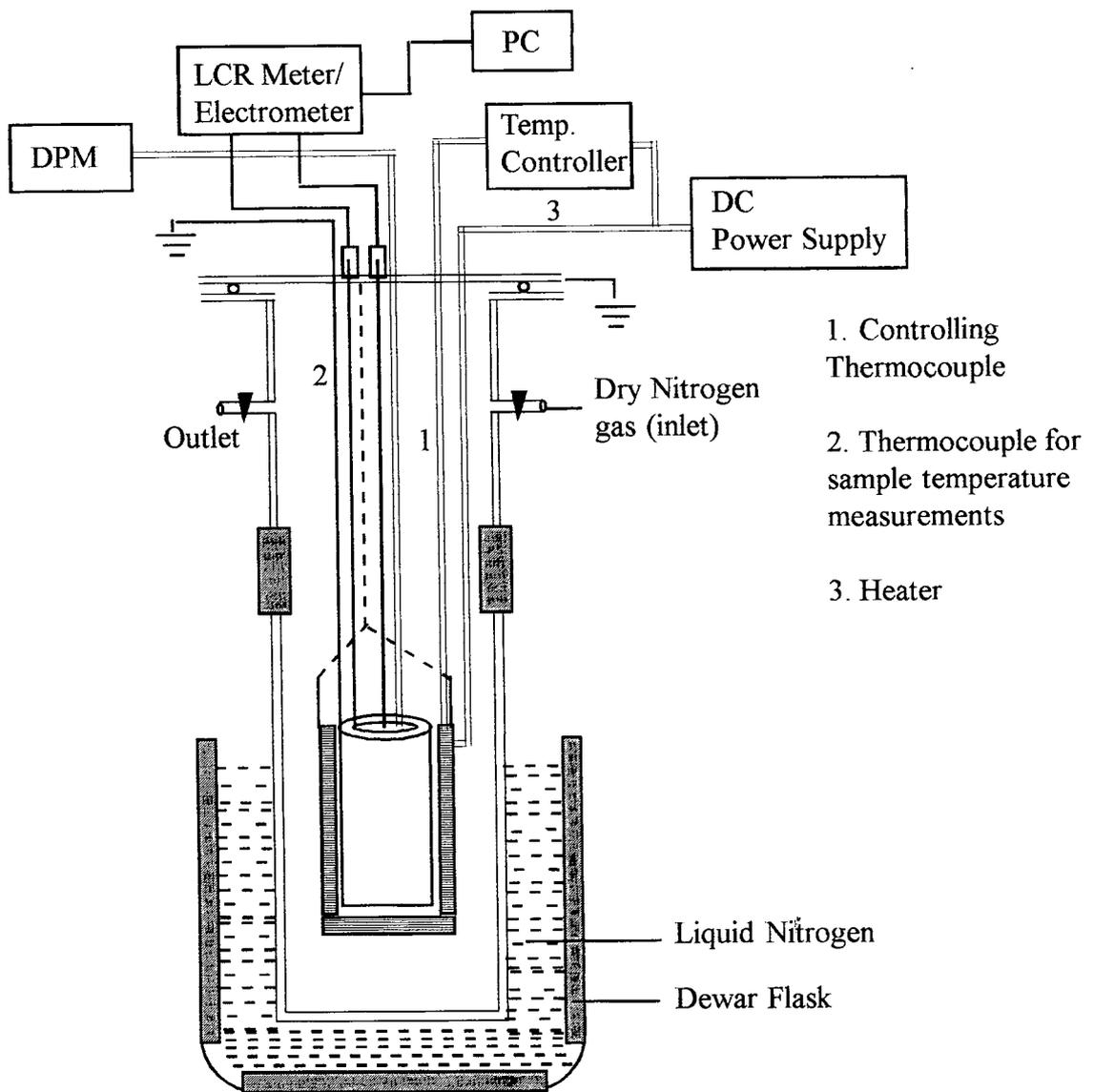


Fig. 2.4: Dielectric measurement set-up for liquid samples.

The sample thermocouple is calibrated at five different temperatures using 'slash bath method'. The accuracy of temperature has been found to be ± 0.5 K. This cell has been heated with the help of a heater around it. The control thermocouple kept near the heater winding monitors the heater temperature and the heater temperature is controlled with the help of a Indotherm-401 temperature controller. ii) A different cell assembly has been used for powdered samples (Figure. 2.5(a)). A disc of about 2.5 cm. in diameter and of about 0.2 cm. in thickness is made out of the sample by pressing it in a pressure dye at a pressure of 10 K bar. The two electrodes are made from silver powder pressed at the same pressure. The sample disc is then pressed between the silver pellets at the same pressure to make the capacitor. This capacitor is held between two brass electrodes with the aid of a light weight spring. The empty cell capacitance of this cell arrangement is usually around 2–4 pF. The sample temperature is measured with the help of Copper-Constantan thermocouple kept deep inside the bottom electrode.

Guard ring is used in the case of solid cell in order to overcome the fringing field at its edges [Figure. 2.5(b)]. When guard ring is used in the solid cell electrostatic field between the plates is perpendicular to the plates even upto the extreme end of edge of the guarded electrode fringing field being transferd to the edges of the guard ring and the effective area of the plates would be the area of the guarded electrode. A formula for the acutal capacitance which corrects for the width of the air gap between plate A and the guard ring given by Maxwell¹⁸ has been used in the calculation.

$$C = \frac{R^2}{4D} + \frac{1}{4} \frac{Rd}{D + 0.22d} \left(1 + \frac{d}{2R}\right) \quad e.s \text{ unit.} \quad (2.9)$$

where R is the radius of the guarded electrode, D the distance between the plates and d is the width of the air gap (all in cms.).

2.2.4 Procedure for the calculation of ϵ' and ϵ''

Before taking measurements, the cell is calibrated¹⁹ with standard liquid namely, Benzene. Lead capacitance has been calculated by measuring total empty cell capacitance

($C_e = C_0 + C_l$) and the total capacitance with the standard liquid ($C_s = C_p + C_l$). The empty cell capacitance C_0 and lead capacitance C_l are calculated from the following formulae:

$$C_0 = \frac{(C_s - C_e)}{(\epsilon' - 1)} \quad C_l = C_e - C_0 = C_e - \frac{(C_s - C_e)}{(\epsilon' - 1)} \quad (2.10)$$

where ϵ' is dielectric constant of benzene at a given frequency. For measurements on sample, the cell is filled with the liquid and kept inside the cryostat for measurements. C_p and D have been measured at different temperatures as a function of frequency and stored on the computer. The real and imaginary parts of complex permittivity have been measured with the help of following formulae:

$$\epsilon' = (C_p - C_l)/C_0; \quad \epsilon'' = D\epsilon' \quad (2.11)$$

Analysis for the determination of the various dielectric constants using appropriate empirical law is done by fitting of ϵ' and ϵ'' to the corresponding law. For this purpose various non-linear fitting programs have been developed which make use of Marquardt-Levenberg least square method²⁰. The separate fitting of ϵ' and ϵ'' yield the same result because of the validity of Kramer-Kronig²¹ relationship. Accuracy of ϵ' is limited by the error in C_0 value and estimated to be upto 3%. The peak loss frequency f_m values are calculated from the parameters using the following equation:²²

$$f_m = f_0 \left[k' / \left\{ \cos(\alpha\pi/2) - \sin(\alpha\pi/2)k' \right\} \right]^{1/(1-\alpha)} \quad (2.12)$$

where $k' = \tan[(1 - \alpha)\pi/2(1 + \beta)]$. The parameters thus evaluated are used for the further analysis as given in the later chapters.

For the ultra low frequency measurements sample is charged with a d.c. source ($V_0 = 100$ V). The discharging current $I(t)$ is digitized at pre-set time intervals. The imaginary part of the dielectric constant is then calculated using Hamon's approximation²³ or using FFT.

For the approximate calculation of high frequency limiting dielectric constant of liquid samples (ϵ_∞) using Eq. (1.28), we measure the refractive index n_D of the samples

using Abbe's refractometer for sodium D -lines. The measurements are based on the observation of the refracted beams passing through the sample and entering a prism of high refracting index at grazing angle, hence, measuring the critical angle r_c which is related with refractive index as: The Abbe's refractometer can measure refractive indices over the range of 1.3 to 1.7 and is provided with a linear scale which can be read to 0.001 and is accurate to 0.0002.

$$n_D = 1/\sin(r_c) \quad (2.13)$$

A drop of the liquid whose refractive index is desired is placed upon the hypotenuse of one of the two prisms, and the hypotenuse of the other prism is placed upon that of first one so that the two prisms together form a cubical block of glass. A telescope is focused for parallel light shows the characteristic divided field. The index of the liquid is then read directly from the calibrated scale. The actual ϵ_∞ can be approximated as $1.05 n_D^2$ taking into account the contribution from atomic polarization.

2.3 X-Ray Diffraction

The X-ray diffraction²⁴ (XRD) pattern was taken for the samples at room temperature using Philips Xpert Diffractometer using CPS 120 Detector. The X-ray unit was monochromatized using Cu K_{α_1} ($\lambda = 1.54056\text{\AA}$) with silicon ($a = 0.357\text{ nm}$) for internal standard. The diffractograms are analyzed for indexing and crystal structure determination using standard software supplied by the manufacturer of the X-ray unit.

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