Experimental Technique

The determination of relaxation times of molecules of polar organic compounds in the liquid state with the help of Debye's equations involves measurements of the dielectric quantities $\epsilon'$, $\epsilon''$, $\epsilon_0, \epsilon_\infty$ and refractive index $n_D$. There are standard methods for measuring these quantities. The theories of the methods of the measurements and the procedures followed in the present investigations are given briefly in the following sections.

1. Measurement of dielectric permittivity $\epsilon'$ and dielectric loss $\epsilon''$ :

The values of $\epsilon'$ and $\epsilon''$ of liquids in 1.62 cm., 3.17 cm and 3.44 cm microwave regions were measured by Surber's[1] method Fig. (1.1 and 1.2) and in some liquids at 3.49 cm microwave region, these are measured by Poley's[2] method Fig.(2).

1.1. Surber's method :

In microwave frequency region measurements to determine the dielectric properties are normally made upon a sample of material which is completely enclosed within a hollow wave guide. The behaviour of the system must be analysed in terms of propagation characteristics of the electromagnetic energy through the dielectric medium.

This method of measurements of $\epsilon'$ and $\epsilon''$ is based upon the variation of reflection coefficient of uniform dielectric layer as the depth of the layer is varied.

Theory :

The propagation constant for air filled guide is given by

$$\gamma_g \approx j\beta = \frac{2\pi j}{\lambda}\sqrt{1-\left(\frac{\lambda}{\lambda_c}\right)^2} \qquad (1.1.1)$$

Similarly the propagation constant for liquid filled guide is

$$\gamma_L \approx \alpha_L + j\beta_L = \alpha_L + \frac{2\pi j}{\lambda_d} = \frac{2\pi j}{\lambda}\sqrt{\epsilon-\left(\frac{\lambda}{\lambda_c}\right)^2} \qquad (1.1.2)$$

where

$\lambda$ = Free space wave length

$\lambda_c$ = Cut off wave length

$\lambda_d$ = wave length in the liquid filled guide

$\alpha_L$ = attenuation in the dielectric

$\beta_L$ = phase constant in the dielectric

$$Z_d = \frac{\gamma_L}{\gamma_g} = \frac{\sqrt{\epsilon-\left(\frac{\lambda}{\lambda_c}\right)^2}}{\sqrt{1-\left(\frac{\lambda}{\lambda_c}\right)^2}} \qquad (1.1.3)$$

Characteristic impedance of the dielectric filled guide to the empty guide.

For a dielectric sample of length $L$, enclosed within a section of wave guide and terminated by a perfectly reflecting short-circuit plane, the magnitude of reflection coefficient $R$ at the face of the dielectric will be given by the equation

$$|R| = \frac{|E^-|}{|E^+|} = \left|\frac{Z_d \tanh \gamma_d L - 1}{Z_d \tanh \gamma_d L + 1}\right| \qquad (1.1.4)$$

where $E^+$ is the incident voltage wave and $E^-$ is the reflected voltage wave in the empty guide.

The output of a square law detector coupled to the reflected wave by a unidirectional coupler is proportional to $|R|^2$ for a constant incident power. For lengths of the dielectric sample which are integral multiples of $\lambda_d/2$ the set of values of may be written in the form

$$|R|^2 = \frac{T + 2Fe^{-2n\alpha_d\lambda_d} + e^{-4n\alpha_d\lambda_d}}{1 + 2Fe^{-2n\alpha_d\lambda_d} + Te^{-4n\alpha_d\lambda_d}} \tag{1.1.5}$$

where $T = |R_\infty|^2 = \left|\frac{Z_d - 1}{Z_d + 1}\right|^2$

$F = (1 - |Z_d|^2)/(1 + |Z_d|^2)$

$L = n\lambda_d$ = length of the sample, so that $n = \frac{1}{2}, 1, \frac{3}{2}, \ldots$ for short circuit termination.

From transmission line theory, the wave length $\lambda_d$ and the attenuation per wave length ( $\alpha_d\lambda_d$ ) in the dielectric is related to $\epsilon'$ and $\epsilon''$ and the dissipation factor $D$ respectively by the following relations

$$\lambda_d = \left[\frac{\lambda^2}{\epsilon' - (\frac{\lambda}{\lambda_c})^2}\right]^{\frac{1}{2}} \left[1 - \tan^2(\tfrac{1}{2}\tan^{-1} D)\right]^{\frac{1}{2}} \tag{1.1.6}$$

$$\alpha_d = \frac{\pi\epsilon''}{\lambda^2}\lambda_d \tag{1.1.7}$$

and

$$\alpha_d\lambda_d = 2\pi\tan(\tfrac{1}{2}\tan^{-1} D) \tag{1.1.8}$$

From equation (1.1.6) and equation (1.1.7) the expressions for $\epsilon'$ and $\epsilon''$ are obtained as

$$\epsilon' = (\frac{\lambda}{\lambda_c})^2 + (\frac{\lambda}{\lambda_d})^2\left[1 - \tan^2(\tfrac{1}{2}\tan^{-1} D)\right] \tag{1.1.9}$$

and

$$\epsilon'' = \frac{1}{\pi}(\frac{\lambda}{\lambda_d})^2(\alpha_d\lambda_d) \tag{1.1.10}$$

Thus for the determination of $\epsilon'$ and $\epsilon''$ of polar liquids, the dissipation factor $D$ and the attenuation per wave length ( $\alpha_d \lambda_d$ ) must be known. They are computed analytically by the method of successive approximations as follows.

Let $M_n$ be the ratio of the nth maximum of the reflected signal for $L = n\lambda_d$ to that for an effectively infinitely long dielectric medium, so that

$$M_n = \frac{|R_n|^2}{|R_\infty|^2} \tag{1.1.11}$$

where $n = \frac{1}{2}, 1, \frac{3}{2}, \cdots\cdots$ etc.

Then, in order to simplify the form of the final equation, define

$$x = \frac{\lambda_d}{\lambda_g} \quad \text{and} \quad y = \frac{1-x}{1+x}$$

Physically, $x$ represents the characteristic impedance of the guide filled with an ideal dielectric having the same $\lambda_d$ and $y$ the corresponding reflection coefficient for an infinitely long column.

Substituting equation (1.1.5) into equation (1.1.11) results in a quadratic equation for $\exp(-2n\alpha_d\lambda_d)$ which may be solved for attenuation per wave length $\alpha_d\lambda_d$ in neper.

$$(\alpha_d\lambda_d) = \left(\tfrac{1}{2}n\right)\ln\left[K_1\left\{1 + (1+K_2)^{\frac{1}{2}}\right\}\right] \tag{1.1.12}$$

where

$$K_1 = \frac{C_1(1 - M_nT)}{M_n - 1} \tag{1.1.13}$$

and

$$K_2 = C_2(M_n-1)(1-M_nT^2)/(1-M_nT)^2 \tag{1.1.14}$$

or, to a first approximation, $K_1$ and $K_2$ may be expressed as

$$K_1 \approx \left(\tfrac{1}{y}\right)(1-y^2M_n)/(M_n-1) \tag{1.1.15}$$

$$K_2 \approx (M_n-1)(1-y^4M_n)/(1-y^2M_n)^2 \tag{1.1.16}$$

The exact expression for $\mathcal{T}$, $C_1$ and $C_2$ are

$$\mathcal{T} = |R_\infty|^2 = \frac{1 - x(1-\frac{x}{2})[1 + \cos(\tan^{-1}D)]}{1 + x(1+\frac{x}{2})[1 + \cos(\tan^{-1}D]}$$

$$\approx y^2 \left[1 + D^2 \left\{ x/(1-x^2)^2 \right\} - \cdots\cdots \right] \tag{1.1.17}$$

$$C_1 = \left|\frac{F}{\mathcal{T}}\right| = \frac{1 - \frac{x^2}{2}[1 + \cos(\tan^{-1}D)]}{1 - x(1-x/2)[1 + \cos(\tan^{-1}D]}$$

$$\approx 1/y \left[1 - \tfrac{1}{2} D^2 \left\{ x(1+x)/(1-x^2)^2 \right\} + \cdots\cdots \right] \tag{1.1.18}$$

$$C_2 = \left|\frac{\mathcal{T}}{F^2}\right| = \frac{1 + x^2 \sin^2(\tan^{-1}D)}{[1 - x^2 \cos^2(\frac{1}{2}\tan^{-1}D)]^2}$$

$$\approx 1 + D^2 \left[ x^2/(1-x^2)^2 \right] - \cdots \tag{1.1.19}$$

The dissipation factor $D$ is then determined by the equation

$$D = \tan\left[2\tan^{-1}(\alpha_d \lambda_d / 2\pi)\right] \tag{1.1.20}$$

The determination of $D$ from the experimental data is then evidently a process of successive approximations, which however, converges very rapidly. For $D \leqslant 0.1$, $K_1$ and $K_2$ may be considered as functions solely of $Y$ and $Mn$ and only one calculation need be made. For a larger value of dielectric loss, the first value obtained for $D$ must be used to recompute $K_1$ and $K_2$ to determine a second, closer approximation for $D$. If $D \leqslant 0.3$ then the approximate form of equations for $\mathcal{T}$, $C_1$ and $C_2$ are to be taken. For $0.3 \leqslant D \leqslant 0.1$ the $D^2$ terms in the approximate equations for $\mathcal{T}$ and $C_1$ are replaced by $4\sin^2(\frac{1}{2}\tan^{-1}D)$ and the $D^2$ terms in the approximate equation for $C_2$ is replaced by $[\sin^2(\tan^{-1}D)]$.

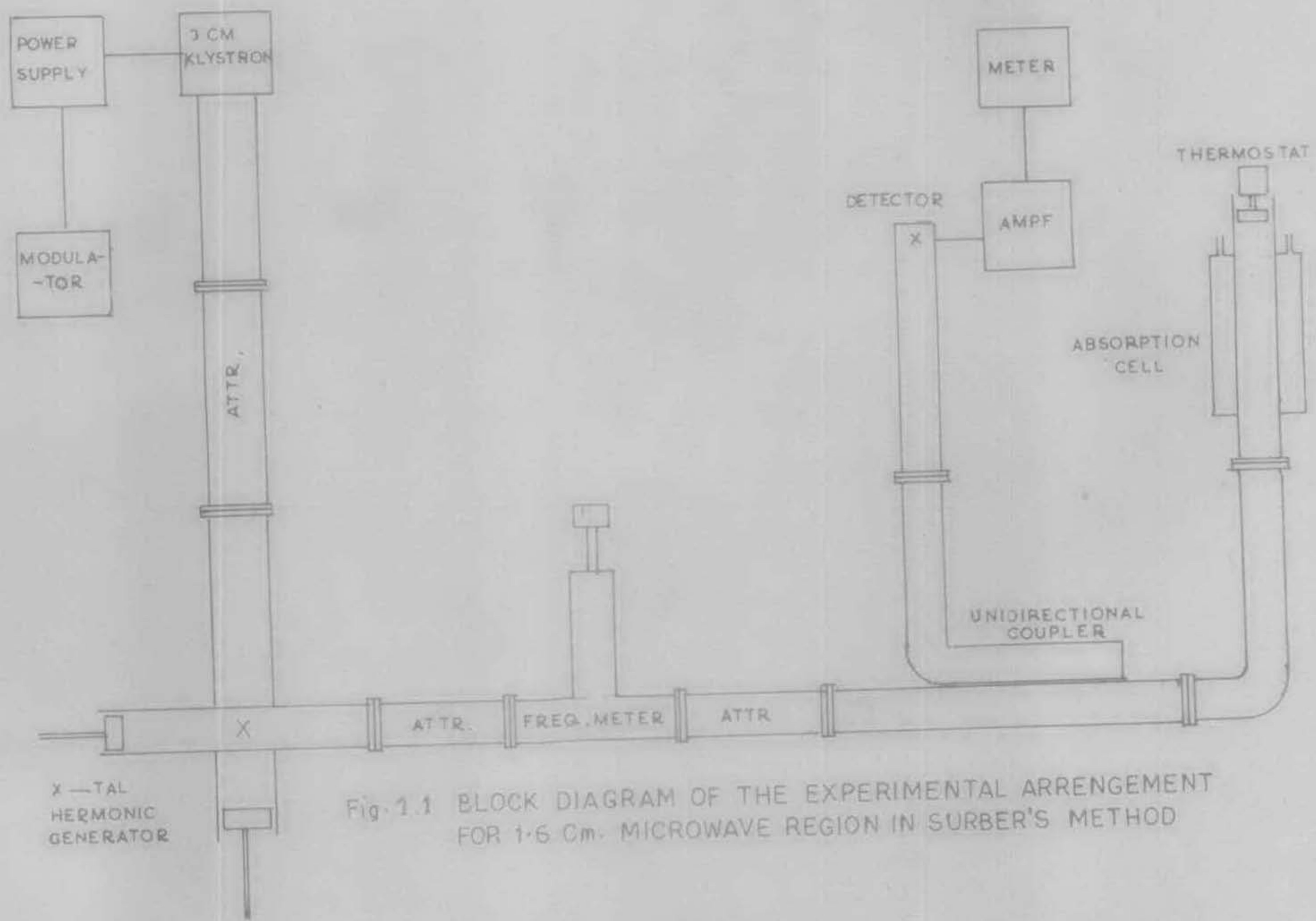


Fig. 1.1 BLOCK DIAGRAM OF THE EXPERIMENTAL ARRENGEMENT FOR 1·6 Cm. MICROWAVE REGION IN SURBER'S METHOD

1.1.1. <u>The actual experimental arrangement</u> :

A block diagram of the experimental units in the microwave region of 1.62 cm, 3.17 cm and 3.49 cm wave lengths used in the present investigation are shown in Figs.(1.1, 1.2) and 2). The general set us of all the units are the same, differing only in the fact that 1.62 cm microwave power was generated from 3 cm power by crystal harmonic generator. Square wave was used to modulate the frequency of the Klystron oscillator of each unit. Attenuators just after the oscillator were used to prevent the frequency pulling of the oscillator. The frequency of the microwave power was measured by the absorption type frequency meter in each unit. At each wave length of operation the liquid cells used were of same general design. They consisted of high quality of silver wave guide terminated at one end by thin teflon window and short circuited at the other by plunger made of silver. The cells were maintained at different temperature by thermostatic arrangement.

The purified liquid was taken in the thermostated dielectric cell which is allowed to attain a constant temperature.

The plunger in the cell is adjusted so that it is at the first minimum adjacent to the teflon window. The length of the dielectric layer is slowly increased by raising the plunger by means of microwave drive mechanism. The output meter reading shows a series of maxima and minima which are noted. When the length of the dielectric is sufficiently large, the output meter reading becomes constant. This reading behaves as infinitely long dielectric.

From the positions of the plunger for successive maxima, the value of $\lambda_d/2$ is obtained. From the maxima values of the output meter reading and the infinity value, the ratio $M$ is obtained. With $\lambda_d$, $M$, the value of $D$ (dissipation factor) is estimated. The values of $\epsilon'$ and $\epsilon''$ are then obtained by successive approximations.

1.2. Poley's method :

This method of obtaining the values of $\epsilon'$ and $\epsilon''$ involves the measurement of the standing wave ratio $\eta$ as a function of length $L$ of the liquid column, which is terminated by short circuiting plunger.

The propagation constant in the air filled guide

$$\gamma_g \approx j\beta = \frac{2\pi j}{\lambda}\sqrt{1-\left(\frac{\lambda}{\lambda_c}\right)^2} \tag{1.2.1}$$

and the propagation in the liquid filled guide

$$\gamma_L \approx \alpha_L + j\beta_L = \frac{2\pi j}{\lambda}\sqrt{\epsilon-\left(\frac{\lambda}{\lambda_c}\right)^2} \tag{1.2.2}$$

The ratio of complex impedance $Z_1$ to that of the air filled guide $Z_0$ is

$$\frac{Z_1}{Z_0} = \frac{\gamma_g}{\gamma_L} = \sqrt{\left\{1-(\lambda/\lambda_c)^2\right\}\Big/\left\{\epsilon-\left(\frac{\lambda}{\lambda_c}\right)^2\right\}} \tag{1.2.3}$$

The relative complex input impedance $Z_i/Z_0$ at the teflon window for short circuit termination

$$\frac{Z_i}{Z_0} = \frac{Z_1}{Z_0}\tanh \gamma_L L \tag{1.2.4}$$

and is related to the standing wave ratio $\eta$ as

$$\eta = E_{max} / E_{min}$$

$$= \frac{1 + \left| \frac{Z_i/Z_0 - 1}{Z_i/Z_0 + 1} \right|}{1 - \left| \frac{Z_i/Z_0 - 1}{Z_i/Z_0 + 1} \right|} \tag{1.2.5}$$

From consideration of transmission line theory, Poley obtained the relation

$$\eta_m / \eta_n = \frac{\tanh(n\pi \tan \Delta/2)}{\tanh(m\pi \tan \Delta/2)} \tag{1.2.6}$$

and

$$\eta_m / \eta_\infty = \frac{1}{\tanh(m\pi \tan \Delta/2)} \tag{1.2.7}$$

where $\eta_m$ and $\eta_n$ are the S.W.R for mth and nth maxima and $\eta_\infty$ is that for an line of infinitely long length.

$$\tan \Delta = \frac{\epsilon''}{\epsilon' - (\frac{\lambda}{\lambda_c})^2} = \text{Wave guide loss} \tag{1.2.8}$$

Poley plotted the graphs of

$$\eta_m/\eta_n \text{ vs } f(\tan \Delta/2)$$

and $\eta_m/\eta_\infty$ vs $f(\tan \Delta/2)$ from the relation of (1.2.6) and (1.2.7).

Knowing the values of $\tan \Delta/2$ from the graphs, $\lambda_t/2$ from the two successive minima of plunger position and output meter reading, free space wave length $\lambda$ and the cut off wave length $\lambda_c$, the values of $\epsilon'$ and $\epsilon''$ are calculated from the

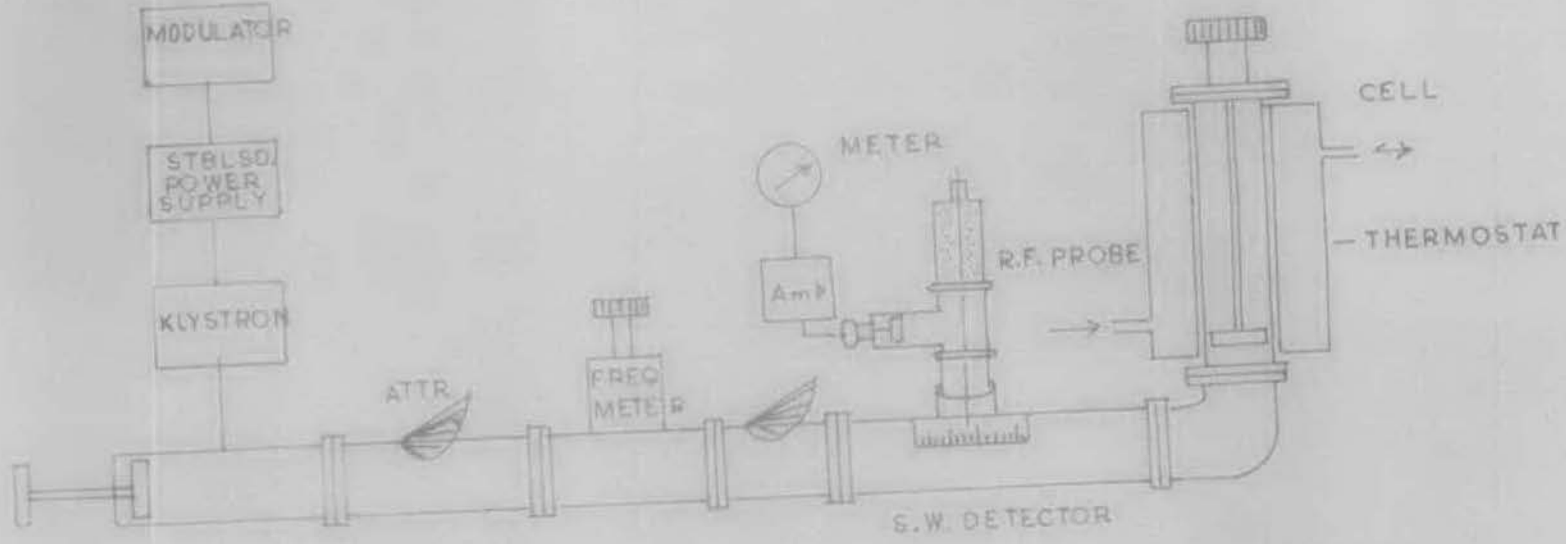


FIG. 2 BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR
3.5 CM IN POLEY'S METHOD

equation

$$\epsilon' = \left(\frac{\lambda}{\lambda_c}\right)^2 + \left(\frac{\lambda}{\lambda_l}\right)^2 \left(1 - \tan^2 \Delta/2\right) \tag{1.2.9}$$

and

$$\epsilon'' = 2\left(\frac{\lambda}{\lambda_l}\right)^2 \tan \Delta/2 \tag{1.2.10}$$

Corrections for losses in walls, junctions and terminations are neglected.

2. Measurement of static dielectric constant $\epsilon_o$ of liquids :

The static dielectric constant of liquids at different temperature were measured by resonance method. A block diagram of the set up made for this purpose is given in Fig.(3). It was determined at 1 MHz from a crystal oscillator. The output of the crystal oscillator is connected to a power amplifier through a buffer amplifier, so that no power is drawn from oscillator and the frequency pulling or output variation is avoided.

The liquid cell was cylindrical vessel of brass in which suspended a solid cylinder of the same metal. The diameter of the solid cylinder was less than that of the inner diameter of the vessel. To avoid any metallic contact between them, the solid cylinder was held there by a polystyrene cap. The inside of the brass vessel and the outside of the solid cylinder was silver plated. The liquids to be investigated were introduced through a small inlet on the upper face of the cap. An outlet was made on the body of the vessel to make a constant level of the liquid inside it. The vessel was fitted with a water jacket through which water at different temperature from a thermostat was made to circulate.

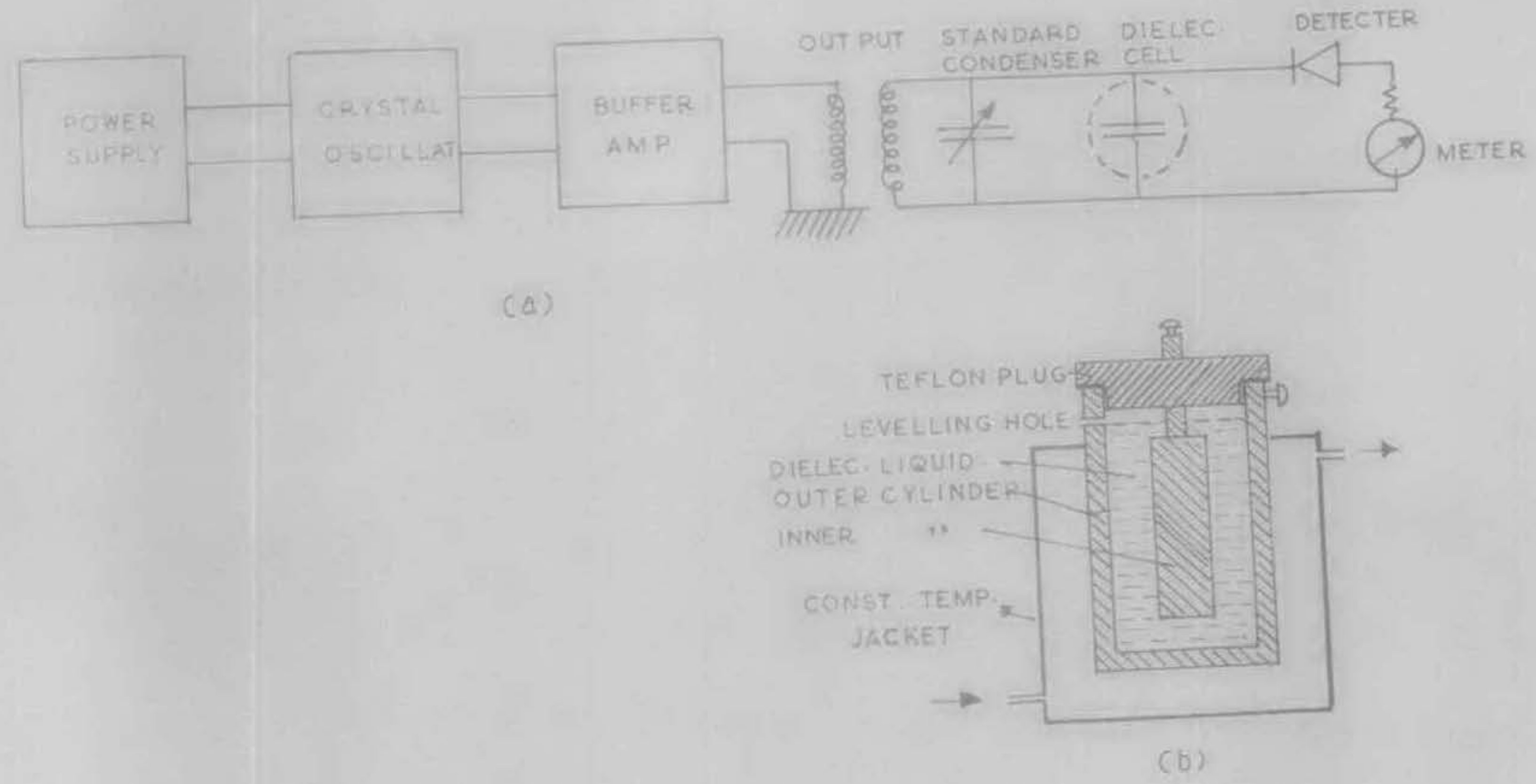


FIG : 3. BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR MEASUREMENT OF STATIC DIELECTRIC CONSTANT.

The dielectric constant is measured by comparing the capacity of the dielectric cell with the liquid as dielectric to the capacity with air as dielectric. The stray capacity was calculated out from the measurement of capacity of the cell filled with some standard liquids as $CCl_4$ or $C_6H_6$ whose dielectric constants were given in the literature. A standard capacity with an accuracy of 0.1 picofarad was used for measurement of capacity. The ratio of the capacity of the cell filled with experimental liquid to that of the empty cell is the dielectric constant of the liquid.

3. Determination of viscosity $\eta$ :

The viscosity of liquids were measured with the help of a Ostwald Viscometer.

The liquids were taken in the viscometer kept immersed in water taken in a flask provided with water jacket. The temperature was maintained constant by means of a thermostat.

The time of fall 't' seconds of the liquid between two fixed marks in the viscometer at any temperature was noted. The density of liquid $\rho$ at that temperature was determined by a picnometer. The viscosity $\eta$ of the liquid at that temperature was given by the relation

$$\eta = \rho\left\{at - \frac{b}{t}\right\} \tag{3.1}$$

where a and b are the two constants of the viscometer determined by the time of fall of water at two different temperature. Knowing the density and viscosity of water at that two particular temperature from critical table, the values of a and b were determined. In this way viscosity of liquids at different temperatures were determined.

4. Refractive index $\eta$ :

The refractive index of the liquids at different temperatures were found out with Abbe's refractometer. The temperature was maintained constant with a thermostat.

5. Purifications of samples :

Pure samples were procured from Schuchardt (Germany), Fluka (Switzerland) and E. Merck (Germany). All these chemicals were dried by dehydrating agents and then were distilled by fractional distillation. The proper fractions were distilled again under reduced pressure before use in the investigations.

6. Standarisation of the dielectric data obtained in the present investigations :

The values of $\epsilon'$, $\epsilon''$, $\epsilon_0$ and $n_D^2$ determined in the present investigation in the case of chlorobenzene, bromobenzene and anisole were found to be in good agreement with respective values reported in literatures[3].

7. Activation energy of dielectric relaxation :

The dielectric relaxation has been treated as a rate process[4] in which polar molecules rotate from one equilibrium position to another. The process of this molecular rotation requires an activation energy sufficient to overcome the energy barrier separating the two equillibrium positions. The number of time such rotations occur per second is given by the rate expression

$$K = \frac{1}{\tau_0} = \frac{kT}{h} e^{-\Delta F_\epsilon / RT} \qquad (7.1)$$

where $\tau_0$ = Most probable relaxation time

$\Delta F_\epsilon$ = Free energy of activation

$= \Delta H_\epsilon - T\Delta S_\epsilon$

$$\text{or } \tau_0 = \frac{h}{kT} e^{\Delta H_\epsilon / RT} e^{-\Delta S_\epsilon / R} \qquad (7.2)$$

where $\Delta H_\epsilon$ is the heat of activation of the dipole relaxation and $\Delta S_\epsilon$ is the entropy of activation.

From the slope of the straight line plot of $\log \tau T$ vs $1/T$ the heat of activation $\Delta H_\epsilon$ for dipole relaxation can be obtained.

8. <u>Activation energy for viscous flow</u> :

The viscosity of liquids may be approached in an analogue manner.

Viscous flow is pictured as the movement of one layer of molecules with respect to another layer, involving translational as well as rotational motion of the molecules with an activation energy required to pass over a hindering potential barrier. The equation for viscosity in terms of this mechanism

$$\eta = \frac{hN}{V} e^{\Delta F_v / RT} \qquad (8.1)$$

where

$\Delta F_v$ = Free energy of activation for viscous flow

$V$ = Molar volume

$$\Delta F_v = \Delta H_v - T\Delta S_v$$

$$\therefore \eta = \frac{hN}{V} e^{\Delta H_v/RT} \cdot e^{-\Delta S_v/R} \qquad (8.2)$$

From the slope of the straight line plot of $\log \eta$ vs $1/T$ the heat of activation for viscous flow can be obtained.

## References

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