CHAPTER II

EXPERIMENTAL TECHNIQUE AND THEORIES OF MEASUREMENT

In the previous chapter the object of the present investigation has been dealt clearly. For putting these objects in the field of application and for achieving the desired result, the techniques adopted and employed for performing the experiment, are described in this chapter.

In order to investigate molecular behaviour of liquids such as

(a) dipolemoments and molecular structure of polar molecules (b) dielectric relaxation phenomena of polar molecules in nonpolar solvents (c) electrical conductivity of critical opalescent mixture near critical temperatures, the following measurements have been made in the laboratory.

(i) Measurement of radio frequency and high frequency conductivity (K') of liquids at different temperatures and concentrations.

(ii) Determination of dipole moment of polar liquids.

(iii) Measurement of coefficient of viscosity (η) at different temperatures.

2.1. Theory of Measurement and Experimental Arrangement for Determining Radiofrequency Conductivity.

A. Theory of Measurement of Radio Frequency Conductivity.

The block diagram of the experimental arrangement can be represented by a simple network circuit as shown in Fig. 2.1.

Let Z_p be the equivalent impedance, then for parallel combination

$$Z_p = \frac{R}{1 + j\omega CR} \qquad \ldots 2.1$$

and the impedance for the series combination

$$Z_s = \left(R' - \frac{j}{\omega C'}\right) \qquad \ldots 2.2$$

From eq. (2.1) and (2.2)

$$R' = \frac{R}{1 + \omega^2 C^2 R^2} \qquad \ldots 2.3$$

and

$$\frac{1}{\omega C'} = \frac{\omega C R^2}{1 + \omega^2 C^2 R^2} \qquad \ldots 2.4$$

and as $\omega^2 C^2 R^2 \gg 1$, then $C' = C$.

Further the resonant current (I_o) with empty glass cell is given by

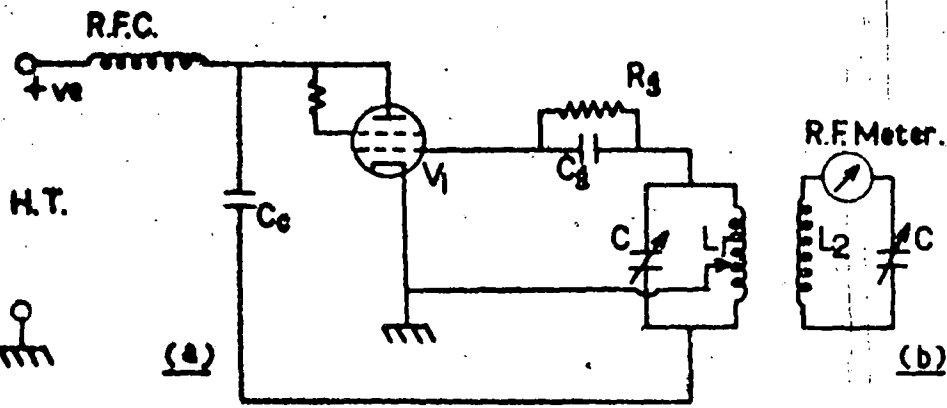$$I_o = \frac{E}{R_o} \qquad \ldots 2.5$$

R.F meter

Thermostat

Oscillator   P

C_V

C_2

$\equiv$

C_0

$C_0 = C_V + C_2$

(a)   COUPLED   CIRCUIT

$\equiv$ C   R $\equiv$ $C' = C$

R'

(b)   (c)

Fig – 2.1   (a) Circuit   arrangement
              (b)and(c) Equivalent circuits.

Fig. 2.2, (a) Radio frequency oscillator.   (b) Secondary tuning circuit.

List of components.

$V_1 = $ 6L.6. $C_c = $ 01 μF.
$R_g = $ 30 kΩ R.F.C.= Radio frequency choke.
$C_g = $ 350 P.F.   R.F.Meter = Radio frequency
$C = $ 0-500 P.F.   milli ammeter.
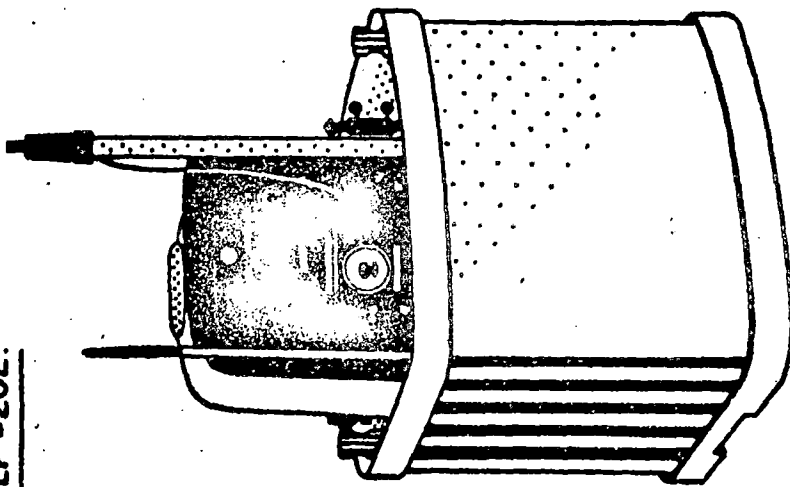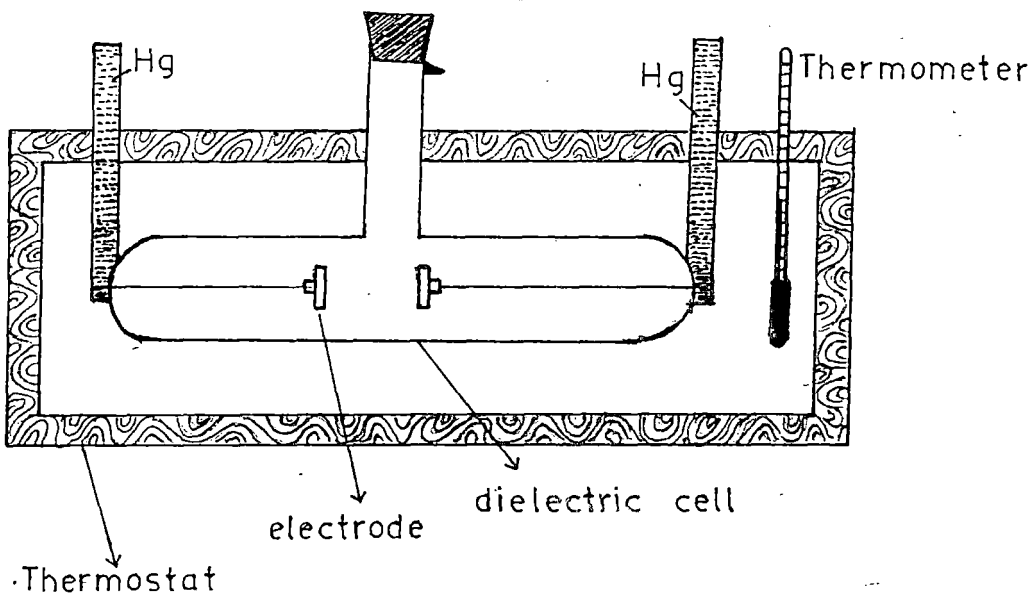

Neo-Thermostat
Type No. LP -202.

FIG. 2.6.

Fig - 2.3

where R_o is the r.f. resistance for the secondary tuning circuit. At the resonance condition the R_o can be represented as

$$R_o = \frac{C_2 - C_1}{2\omega C_1 C_2} \left(\frac{I_1^2}{I_o^2 - I_1^2} \right)^{1/2} \qquad \ldots 2.6$$

where I_o is the resonant current, C_1 and C_2 are the lower half power and upper half power point capacitance respectively, that is at the resonance current $I_1 = 0.707$ of I_o. The capacitance were measured by the help of a LCR bridge (Model No. Universal bridge, No. 2700, Marconi, Instruments Ltd.).

Again when the cell is filled with dielectric liquid, the resonant current becomes I_2 and is given by

$$I_2 = \frac{E}{R_o + R'}$$

or $$I_2 = \frac{E}{R_o + \dfrac{R}{1 + \omega^2 C^2 R^2}} \qquad \ldots 2.7$$

If we call $\dfrac{I_o}{I_2} = \alpha$, then from eq. (2.5) and eq. (2.7) we get the radio frequency resistance

$$R = \frac{1 \pm \sqrt{1 - 4 R_o^2 (\alpha - 1)^2 \omega^2 C^2}}{2 R_o (\alpha - 1) \omega^2 C^2} \qquad \ldots 2.8$$

In the present experimental set up

$$4R_o^2 (\alpha -1)^2 \omega^2 c^2 \ll 1$$

then r.f. resistance of dielectric liquid

$$R = \frac{1}{R_o \omega^2 c^2 (\alpha -1)} \qquad \ldots 2.9$$

But we know resistance

$$R = \rho \frac{l}{S}$$

when ρ is the specific resistance, l is the electrode distance and S is the cross sectional area of the electrodes.

If K' is the conductivity of the dielectric then K' can be written as

$$K' = \frac{1}{\rho}$$

or,

$$K' = \frac{l}{S R} \qquad \ldots 2.10$$

Since the cell is a parallel plate condenser thus the capacitance of the cell can be written as

$$C = \frac{S}{2 \pi l} \qquad \ldots 2.11$$

Therefore the r.f. conductivity can be expressed

as

$$K' = \frac{1}{4\pi RC} \qquad \qquad \dots 2.12$$

This is the fundamental formula for measuring the radio frequency conductivity of the dielectric liquids.

B.   The Ultra High Frequency and Microwave conductivity (K_{ij}) of the polar liquid dielectrics in non polar solvent were calculated from the experimental value of dielectric loss factor (ϵ''_{ij}) and dielectric constant (ϵ'_{ij}) at the centimeter wave length region.

As we know from Murphy and Morgan relation that high frequency conductivity is $K_{ij} = K'_{ij} + jK''_{ij}$ where $K'_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi}$ is the real part and $K''_{ij} = \frac{\omega \epsilon'_{ij}}{4\pi}$ is the imaginary part of the conductivity. The magnitude of high frequency conductivity can be calculated from the relation

$$K_{ij} = \frac{\omega}{4\pi} \sqrt{\epsilon'^2_{ij} + \epsilon''^2_{ij}} \qquad \qquad \dots 2.13$$

where ω is the angular frequency $= 2\pi f$.

The complex dielectric constant of the solution can be written as

$$\epsilon^*_{ij} = \epsilon'_{ij} - j\epsilon''_{ij} \qquad \qquad \dots 2.14$$

the imaginary part ϵ_{ij}'' which is the dielectric loss is responsible for absorption of electrical energy to give the resistance to polarisation. But at dilute solution, under the application of microwave electric field it can be consider as $\epsilon_{ij}' \gg \epsilon_{ij}''$. Therefore microwave conductivity of the solution becomes,

$$K_{ij} = \frac{\omega}{4\pi} \epsilon_{ij}' \qquad as \qquad \epsilon_{ij}' \gg \epsilon_{ij}''$$

Considering Debye equation (1.36, 1.37) we can write

$$\epsilon_{ij}' = \epsilon_{ij\infty} + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \qquad \text{... 2.15}$$

$$\epsilon_{ij}'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \cdot \omega\tau \qquad \text{... 2.16}$$

Therefore at h.f. region assuming $\epsilon_{ij}' \gg \epsilon_{ij}''$ eq.(2.15) can be written as

$$\epsilon_{ij}' = \epsilon_{ij\infty} + \frac{\epsilon_{ij}''}{\omega\tau} \qquad \text{... 2.17}$$

where $\epsilon_{ij\infty}$ is the optical dielectric constant of the solution. Therefore at infinite dilute solution h.f. conductivity (K_{ij}) becomes the form

$$K_{ij} = K_\infty + \frac{K_{ij}'}{\omega\tau_s} \qquad \text{... 2.18}$$

where K_∞ is a constant and τ_s is the relaxation time of the solute molecule in solution.

2.2. Theory of Determination of Dipole Moment:-

To calculate the dipole moment of polar solute in non polar solvent we consider the eq. (1.72) as

$$K'_{ij} = \left(\frac{\epsilon_{ij}+2}{3}\right)^2 \cdot \frac{NC_j \mu_j^2}{3kT} \cdot \frac{\omega^2\tau}{1+\omega^2\tau^2}$$

or,

$$K'_{ij} = \frac{\mu_j^2 N\rho_i F_i}{3M_j kT} \cdot \frac{\omega^2\tau_s}{1+\omega^2\tau_s^2} W_j \qquad \dots 2.19$$

where μ_j is the dipole moment of polar solute, N is the Avogadro's number, k is the Boltzmann constant $C_j = \dfrac{\rho_i W_i}{M_j}$ where M_j is the molecular weight of the solute, W_j is the weight fraction, ρ_i is the density of the solvent at infinite dilution, F_i = is the local field of the solvent at infinite dilution = $\left(\dfrac{\epsilon_i+2}{3}\right)^2$, ϵ_i is the static dielectric constant of the solvent and τ_s is the relaxation time of the solute.

Since K'_{ij} is a function of W_j so we have from eq. (2.18),

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j\to 0} = \omega\tau_s\left(\frac{dK_{ij}}{dW_j}\right)_{W_j\to 0} = \omega\tau_s\beta \qquad \dots 2.20$$

where β is the slope of $K_{ij} - W_j$ curve at $W_j \to 0$.

Now from eq. (2.19) and eq. (2.20)

$$\frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \cdot \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} = \omega \tau_s \beta$$

$\therefore$ Dipole moment

$$\mu_j = \left[\frac{3 M_j k T \, (1 + \omega^2 \tau_s^2) \beta}{N \rho_i F_i \omega} \right]^{1/2} \qquad \ldots 2.21$$

Eq. (2.21) is used to calculate the dipole moment of polar solute in non polar solvent.

2.3a. Activation Energy for Dipole Rotation:

The dielectric relaxation has been treated as a rate process in which polar molecule rotate from one equilibrium position to another.

Eyring identifies K, the number of times per second that a dipole acquires sufficient energy to pass over the potential barrier from one equilibrium position to the other, with $1/\tau'$ where τ' is the (microscopic) relaxation time. Therefore, the relaxation time is given by the rate expression

$$\tau' = \frac{h}{kT} \exp\left(\frac{\Delta F_\tau}{RT}\right) \qquad \dots 2.22$$

where h is the Planck constant, k is the Boltzmann constant, T is the absolute temperature, R is the universal gas constant and ΔF_τ is the free energy of activation for dipole relaxation.

since
$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \qquad \dots 2.23$$

Therefore,

$$\tau' = \frac{h}{kT} \exp\left(-\frac{\Delta S_\tau}{R}\right)\exp\left(\frac{\Delta H_\tau}{RT}\right) \qquad \dots 2.24$$

where ΔH_τ and ΔS_τ are the molar enthalpy and molar entropy of activation for dipole relaxation respectively. ΔH_τ is obtained from the slope of the curve obtained by plotting $\ln(\tau'T)$ against $1/T$. Knowing ΔH_τ and τ', ΔS_τ can be calculated from the eq. (2.24).

2.3b. Activation Energy for Viscous Flow:

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

Viscous flow is prefered as movement of one layer of molecules with respect to another layer,

involving translation as well as rotational motion of molecules with an activation energy to pass over a potential barrier. The equation for viscosity terms of this mechanism may be written as

$$\eta = \frac{hV}{N} \, e^{\Delta F\eta / RT} \qquad \qquad ... \ 2.25$$

where $\Delta F\eta$ is the free energy of activation for viscous flow, h the Planck constant, N the Avogadro's number and V is the molar volume and

$$\Delta F_\eta = \left[\Delta H_\eta - T\Delta S_\eta \right] \qquad \qquad ... \ 2.26$$

Then eq. (2.25) may be written as

$$\eta = B \left(e^{\Delta H\eta / RT} \cdot e^{-\Delta S_\eta / R} \right) \qquad \qquad ... \ 2.27$$

where $B = \frac{hN}{V}$, $\Delta H\eta$ the heat activation energy for viscous flow and ΔS_η the entropy of activation for viscous flow.

2.4. Theory of Least Square Fit Method:

It is described to fit a straight line or a parabolic equation to a set of experimental data $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$.

In case of straight line equation for each value of x there are two values of y the actual value y and the value y' predicted by the fitting straight line

$$y = a + bx \qquad \ldots 2.28$$

some deviations

$$d_i = y_i - y_i' = y_i - \left(a + bx_i \right) \qquad \ldots 2.29$$

are positive, others are negative. The squares are all positive. We consider that line as the line of best fits which minimise the sum of squared deviations.

$$f\left(a,b \right) = \sum_{i=1}^{n} \left(y_i - a - bx_i \right)^2 \qquad \ldots 2.30$$

To find the suitable values of a, b for this purpose, we write,

$$\frac{\partial f}{\partial a} = 0 \, , \quad \text{i.e.} \quad na + b\sum x_i = \sum y_i \qquad \ldots 2.31$$

and

$$\frac{\partial f}{\partial b} = 0 \, , \quad \text{i.e.} \quad a\sum x_i + b\sum x_i^2 = \sum x_i y_i \qquad \ldots 2.32$$

By solving these equations (2.31) and (2.32) we can
get a and b. Putting the values of constants a and
b in eq. (2.28) we get the desired fitted striaght line
equation.

Now in the case of parabolic equation

$$a + bx + cx^2 = y \qquad \ldots 2.33$$

We can get the values of the constant a, b and c
by solving the following equations,

$$na + b\sum x_i + c\sum x_i^2 = \sum y_i \qquad \ldots 2.34$$

$$a\sum x_i + b\sum x_i^2 + c\sum x_i^3 = \sum x_i y_i \qquad \ldots 2.35$$

$$a\sum x_i^2 + b\sum x_i^3 + c\sum x_i^4 = \sum x_i^2 y_i \qquad \ldots 2.36$$

Then the required fitted parabolic equation may be
obtained by putting the values of a, b and c in
the equation (2.33).

2.5.   Determination of coefficient of Viscosity
        of the Liquid:

The coefficient of viscosity of liquids at
different temperatures were measured by the help of
Ostwald's viscometer. The viscosity η of the
liquid at a desired temperature was calculated from

the relation

$$\eta_1 = \eta_2 \, \frac{d_1 t_1}{d_2 t_2} \qquad \qquad \ldots 2.37$$

where η_2 is the coefficient of viscosity of a standard liquid (water) d_1 and d_2 are the densities. The time of fall t_1 and t_2 of the investigating liquid and standard liquid (water) were noted by the help of a high precession stop watch at the desired temperature.

2.6. Purification of Liquids:

The purity of liquids are very important factor to the study of molecular behaviour of dielectric liquid. In the present work, we have used pure quality of chemicals which we have obtained from reputed manufacturing companies, namely E.Merck, British Drug House (B.D.H.).

2.7. Washing and Cleaning of the Dielectric Cell:

Initially the glass cell, tube and other glass wares were thoroughly washed with dilute chronic acid and after that these are thoroughly washed with NaOH solution and then washed several times with distilled water.

To remove traces of water, the wash glass wares
and instruments were kept inside the thermostat.
The dried glass instruments and wares were again
washed with dehydrated pure benzene and then
dried.