

CHAPTER II

THE SCOPE AND THE OBJECTIVES OF THE PRESENT WORKS ALONG WITH THE
EXPERIMENTAL TECHNIQUES AND THEORIES OF MEASUREMENTS.

2A.1 THE SCOPE AND THE OBJECTIVES OF THE PRESENT WORKS

The brief review of the earlier theoretical and experimental works on electrical conductivity and dielectric relaxation phenomena of pure polar liquids and polar-nonpolar liquid mixtures, as discussed in chapter I, indicates the possibility of obtaining various valuable information regarding the state of the systems of polar-nonpolar liquid mixtures. The present position of investigation of the dielectric relaxation process of polar-nonpolar liquid mixtures is thus very interesting and encouraging.

Various methods have been reported for determination of dielectric relaxation parameters such as relaxation time τ , dipole moment μ etc of polar liquids in the pure as well as in dilute solution of non-polar solvent. But the methods often invite a slight personal judgement in order to locate exact value of the desired parameters (Guha et al 1977). The process of derivation of dipole moments μ from uhf conductivity measurements shows that the relaxation time τ plays a significant role in yielding the proper value of μ of polar liquids (Ghosh and Acharyya 1977).

Datta et al (1981) used the real part of hf conductivity K'_{ij} of polar-nonpolar liquid mixtures as deduced by Ghosh and Acharyya (1977) to obtain the relaxation time of polar molecule

from the following equation

$$\frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} = \frac{\beta}{R' \omega} = b(\text{say}) \dots\dots\dots(2.1)$$

Where β is the slope of $K'_{ij} - \omega_j$ curve at infinite dilution i.e.

$$\omega_j \rightarrow 0 \text{ and } R' = \frac{\mu_j^2 N \rho_i F_i}{3M_j k T} = \text{constant.}$$

Eq. (2.1) is a quadratic equation of $\omega \tau_s$, thus yielding the value of τ_s from the equation

$$\tau_s = \frac{1}{\omega} \left[\frac{1 \pm 4b^2}{2b} \right] \dots\dots\dots(2.2)$$

The τ_s of eq (2.2) depends mainly upon the value of b . It is single valued for $b \geq 0.5$, but both the values of τ_s will be real and different for $b < 0.5$ (Datta et al 1981).

In recent years (Acharyya et al 1982, Acharyya and Chatterjee 1985, Acharyya et al 1986) it was shown that the ultra high frequency conductivity K_{ij} of polar-nonpolar mixture is given by

$$K_{ij} = \frac{\omega}{4\pi} (\epsilon'_{ij}{}^2 + \epsilon''_{ij}{}^2)^{1/2} \dots\dots\dots(2.3)$$

Where ϵ'_{ij} and ϵ''_{ij} are the real and the imaginary parts of complex dielectric constant ϵ^*_{ij} and $\epsilon'_{ij} \gg \epsilon''_{ij}$.

In the hf region it can be shown that $\epsilon'_{ij} = \epsilon_{ij\alpha} + \epsilon''_{ij} / \omega \tau_s$

$$\text{or, } \frac{\omega}{4\pi} \epsilon'_{ij} = \frac{\omega}{4\pi} \epsilon_{ij\alpha} + \frac{\omega}{4\pi} \epsilon''_{ij} / \omega\tau_a$$

$$\text{or, } K''_{ij} = K_{\alpha} + K'_{ij} / \omega\tau_a \dots\dots\dots(2.4)$$

Murthy et al (1989) pointed out that the methods of Acharyya and Chatterjee (1985) determines τ_a or μ with the prior knowledge of one of the two. They (1989) subsequently presented a procedure for finding out both μ and τ without any prior knowledge of the either quantity. For low concentration of polar solute in non-polar solvent, the variation of K'_{ij} and K''_{ij} with concentration will be linear. Hence from eq. (2.4) the slope of linear plot $K''_{ij} - K'_{ij}$ is $1/\omega\tau_a$ from which τ_a can be calculated. In the low concentration region since K_{α} is constant and $K''_{ij} \approx K'_{ij}$ one can have from eq(2.4)

$$\left[\frac{d K''_{ij}}{d W_j} \right]_{W_j \rightarrow 0} = \omega \tau_a \left[\frac{d K'_{ij}}{d W_j} \right]_{W_j \rightarrow 0} = \omega \tau_a \beta \dots\dots\dots(2.5)$$

The real part of uhf conductivity K'_{ij} of polar-nonpolar liquid mixture is given by (Ghosh and Acharyya 1977)

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j k T} \left[\frac{\omega^2 \tau_a}{1 + \omega^2 \tau_a^2} \right] \omega_j \dots\dots\dots(2.6)$$

Differentiating eq.(2.6) with respect to ω_j and with eq. (2.5) one finally can get,

$$\mu_j = \left[\frac{3M_j k T}{N \rho_i F_i} \frac{\beta}{b \omega} \right]^{1/2} \dots\dots\dots(2.7)$$

where $b = 1 / (1 + \omega^2 T^2)$

The procedure, as mentioned above, is a very simple and straight forward one. It opens a new area to evaluate τ_e and μ of polar molecules dissolved in non-polar solvent. The accurate values of τ_e and μ_j of a polar molecule are necessary as they throw much light on the structure of the molecule. This simple procedure is used extensively in some systems of amides dissolved in different non-polar solvents to find out τ_e and μ_j to realise their structure in the solutions. The study, thus made, has been placed in chapter III .

The study of binary polar mixture in a non-polar liquid is of special interest and it requires the determination of relaxation time τ_{ij} and dipole moment μ_{ij} . The theory used under such study has been first presented in this thesis to find out the dielectric relaxation parameters of a large number of systems viz N,N - dimethyl formamide (DMF) with N,N - tetramethyl urea (TMU) and N,N - dimethyl acetamide (DMA) in benzene. The similar study has been again made for DMF with (i) methyl alcohols (MeOH), (ii) acetonitrile (AN) and (iii) acetone (AC) polar mixtures in benzene. The dipole moments μ_{ij} of the polar mixture at different mole fractions X_j of DMF at 15°C and that of (1:1) mixtures at different temperatures have been measured only to

locate the existence of various types of molecular associations. Such studies for a large number of dielectric liquids including amides have been presented in chapter IV and V.

The accurate determination of relaxation time τ_{ik} and μ_{ik} offers a deep insight of the molecular behaviour of binary polar mixture in a non - polar solvent. Such study very often indicates the presence of various types of molecular associations. There are some theoretical relations (Modan 1987, Yadav and Gandhi 1993) to compute τ_{mix} of binary polar mixture, but these relations are not found to be applicable in case of associated mixtures of two polar liquids in a non - polar solvent. A theoretical relation to calculate τ_{jk} of both associative polar mixture in non - polar solvent has been suggested. The relation and its results on forty one systems of six polar mixtures have presented in chapter VI.

Some highly nonspherical polar molecules like disubstituted benzene, aniline etc. are in the habit to show double relaxation phenomenon having relaxation time τ_1 and τ_2 due to the rotation of small flexible unit attached to the parent ring and the end - over - end rotation of the whole molecule respectively. Bergmann et al (1960) offered a graphical method within the frame work of Debye model to determine τ_1 and τ_2 using the equations

$$\frac{\epsilon'_0 - \epsilon'_\alpha}{\epsilon'_0 - \epsilon'_\alpha} = C_1 \frac{1}{1 + \omega^2 \tau_1^2} + C_2 \frac{1}{1 + \omega^2 \tau_2^2} \dots\dots(2.8)$$

and

$$\frac{\epsilon''}{\epsilon'_0 - \epsilon'_\alpha} = C_1 \frac{\omega\tau_1}{1 + \omega^2 \tau_1^2} + C_2 \frac{\omega\tau_2}{1 + \omega^2 \tau_2^2} \dots\dots(2.9)$$

where C_1 and C_2 are the relative contribution of τ_1 and τ_2 in the relaxation process and $C_1 + C_2 = 1$.

The Kasta et al (1969) subsequently modified the equations of Bergmann et al (1960) and obtained the equations to determine τ_1 and τ_2 from the dielectric relaxation measurements at two given frequencies of electric field of microwave region. An alternative method has been developed in which single frequency measurements of ϵ' , ϵ'' , ϵ_0 and ϵ_α for a polar molecule in a non-polar solvent are enough to estimate τ_1 , τ_2 and C_1 . This method is very simple and provides easy measurements of dielectric relaxation data at a single frequency of electric field to compute τ_1 and τ_2 and hence μ_1 and μ_2 . The chapter VII presents this work in fifteen highly nonspherical polar molecules of which eleven showed double relaxation phenomena.

The works on the pure polar liquid as well as polar liquid in non-polar solvent have provided information on the effects of molecular size and shape upon dielectric relaxation. It also helps to understand the effect of viscosity on the process of dielectric relaxation of polar molecules. In the Debye (1929) treatment the relation between relaxation time and viscosity is

given by $\tau = 4\pi a^3 \eta / kT$. This expression has been applied with the varying degree of success or failure using the value of direct measured macroscopic viscosity η . The validity of the Debye relation has been established in the low viscosity range. With a view of gaining more information in this area, a careful study has been made on the applicability of Debye equation in pure and dilute solution of nitrobenzen in benzen at various concentration and temperature from radio frequency conductivity measurements. This study has been presented in Chapter VIII. In connection of the work, described in chapter VIII, a further study has been done on the variation of conductivity and relaxation time of nitrobenzene at radio frequency electric field with the variation of viscosity produced either by changing temperature or by increasing the viscosity of the solution by gradually adding high viscosity paraffin solvent at room temperature.

2B. Experimental technique and Theories of Measurements

The objectives of the present investigation has been dealt clearly in the first part of the chapter. For putting these objectives in the field of application and achieving the desired results, the techniques adopted and employed for performing the experiment are described here.

2B.1. Theory of Measurement and Experimental Arrangement for Determination of Radio Frequency Conductivity

The principle used in this experimental arrangement is a variant of the resonance method of measuring the dielectric constants. The block diagram of the experimental arrangement is represented by a simple network circuit as shown in Fig.2.1. The dielectric cell used is a cylindrical glass tube fitted with two circular metal electrodes. The dielectric cell is connected in parallel to a tuning condenser as shown in Fig.2.2.

From the network circuit (Fig.2.1) the expression of the equivalent impedances for parallel and series combinations are given by

$$Z_p = \frac{R}{1 + j\omega CR} \dots\dots\dots(2.10)$$

and $Z_p = R' + \frac{1}{1 + j\omega CR}$ \dots\dots\dots(2.11)

respectively.

From eqn (2.10) and (2.11) and considering only real parts one can get

$$R' = \frac{R}{1 + \omega^2 C^2 R^2} \dots\dots\dots(2.12)$$

Further, the resonant current I_o without glass cell is

$$I_o = \frac{E}{R_o} \dots\dots\dots(2.13)$$

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

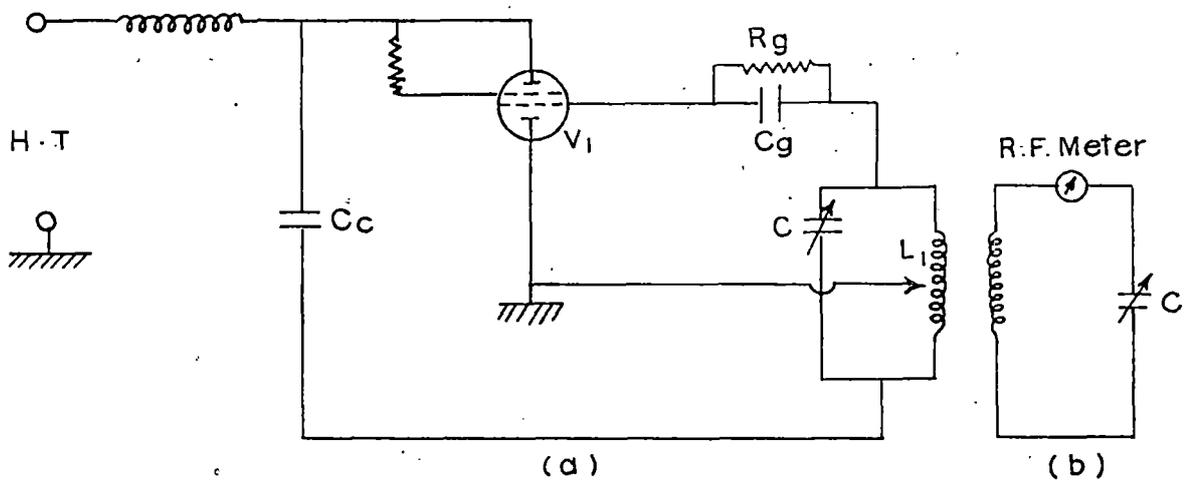


Fig. 2.2 (a) Radio frequency oscillator (b) Secondary tuning circuit.

List of components

$V_1 = 6L.6$

$R_g = 30\text{ K}\Omega$

$C_g = 350\text{ PF}$

$C = 0-500\text{ PF}$

$C_c = 0.01\ \mu\text{F}$

RFC = Radio frequency choke

R.F Meter = Radio frequency
milli ammeter.

$$R_o = \frac{C_2 - C_1}{2\omega C_1 C_2} \sqrt{\frac{I_1^2}{I_o^2 - I_1^2}} \dots\dots\dots(2.14)$$

Where I_1 is the resonant current with empty cell, C_1 and C_2 are the capacities for reducing the resonant current I_o by $1/\sqrt{2}$. The capacitances were measured with the help of a LCR bridge (Model No Universal bridge, No - 2700, Marconi Inc Ltd)

Again when the cell is filled with the dielectric liquid, the resonant current becomes I_2 where

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

or $I_2 = \frac{E}{R_o + \frac{R}{1 + \omega^2 C^2 R^2}} \dots\dots\dots(2.15)$

Putting $I_1/I_2 = \alpha$, from eqs (2.13) and (2.15) the radio frequency resistance becomes

$$R = \frac{1 \pm \sqrt{1 - 4R_o^2 (\alpha-1)^2 \omega^2 C^2}}{2R_o (\alpha-1) \omega^2 C^2} \dots\dots\dots(2.16)$$

In the present experimental set up since $4R_o^2 (\alpha-1)^2 \omega^2 C^2 \ll 1$, we have the r.f. resistance of dielectric liquid from eq. (2.16) as

$$R = \frac{1}{R_o \omega^2 C^2 (\alpha-1)} \dots\dots\dots(2.17)$$

But we know resistance $R = \rho \frac{L}{S} \dots\dots\dots(2.18)$

Where ρ is the specific resistance, l is the distance between the electrodes of cross sectional area S .

If K' is the conductivity of the dielectric liquid, then

$$K' = \frac{1}{\rho} = \frac{l}{SR} \dots\dots\dots(2.19)$$

The capacity of tuning condenser for the resonant current I_0 is

$$C_0 = \frac{S}{4\pi l} \dots\dots\dots(2.20)$$

Therefore, the r.f. conductivity can be expressed as

$$K' = \frac{1}{4\pi RC_0} \dots\dots\dots(2.21)$$

This is the fundamental formula for measuring the r.f. conductivity of dielectric liquid.

2B.2 Washing and Cleaning of Dielectric Cell

The dielectric cell used is a cylindrical glass tube fitted with two circular electrodes separated by a distance. Initially the glass cell, tube and other glass wares were thoroughly washed with dilute chromic acid then with NaOH solution. After washing several times with distilled water, the washed glass wares and instruments were kept inside the thermostate for some hours in order to remove the traces of water. The dried glass instruments and wares were again washed with dehydrated pure benzene and then made dried.

2B.3 Purification of Liquids

The purity of dielectric liquids are very important factor for the study of their molecular behaviour and structure. In the present work, pure quantity Analar grade liquids, obtained from reputed manufacturing companies viz. E, Mark, British Drug House (B.D.H.) etc have been used. The liquids were distilled in vacuum and kept in a desiccator before it was taken in the dielectric cell.

2B.4. Determination of Coefficient of Viscosity

The coefficient of viscosity of liquids at different temperatures were measured with the help of Ostwald's viscometer. The viscosity η of the liquid at a desired temperature was calculated from the relation $\eta = \eta' \frac{dt}{dt'}$ where η' is the coefficient of viscosity of standard liquid (water), d and d' are the densities of the dielectric liquid and standard liquid respectively. The time of fall t and t' of the investigating liquid and the standard liquid (water) were noted with the help of a high precession stop watch at the desired temperature.

REFERENCES

Acharyya S and Chatterjee A K (1985): Ind J Pure & Appl Phys
23 484

Acharyya S, Chatterjee A K, Acharyya P and Saha I L (1982):
Indian J Phys **56** 291

Acharyya C R, Chatterjee A K, Sanyal P K and Acharyya S
(1986): Ind J Pure & Appl Phys **24** 234

Bergmann K, Roberti D M and Smyth C P (1960): J Phys Chem **64** 665

Datta S K, Acharyya C R, Saha I L and Acharyya S (1981): Indian J
Phys **55B** 140

Debye P (1929): Polar Molecules, Chemical Catalogue, New York

Ghosh A K and Acharyya S (1977): Indian J Pure & Appl Phys
15 667

Kastha G S, Datta J, Bhattacharyya J and Roy S B (1969): Indian J
Phys **43** 14

Madan M P (1987): J Mol Liq. (Netherlands) **33** 203

Murthy M B R, Patil R L and Deshpande D K (1989): Indian J Phys
63B 491

Yadav J S and Gandhi J M (1993): Ind J Pure & Appl Phys **31** 489